derived from these parameters also are presented. The root-mean-square deviation between the observed rate coefficients and those calculated using the "best" values of enthalpy and entropy of activation is ~2.0%.

TABLE I

FIRST-ORDER RATE COEFFICIENT

$$k = -\frac{\Delta \ln [\mathrm{CrBr}^{2+}]}{\Delta t}$$

FOR AQUATION OF BROMOCHROMIUM(III) ION[a]

$I = 1.00\ M$

$[\mathrm{H}^+]$, M	$10^5k \times$ sec.		
	30°	45°	60°
0.056	4.40		
0.060		34.0	
0.070	3.77		216.
0.080		27.8	
0.100	2.32[b]	22.6	161.
0.160	2.15	16.7	113.
0.300	1.59	11.4	74.5
1.00	1.01	7.40	44.9

[a] The initial concentration of bromochromium(III) ion ranged from 0.0085 to 0.014 M. The solutions contained zinc ion at a concentration less than half the initial concentration of bromochromium(III) ion. [b] Omitted for correlations to obtain ΔH^* and ΔS^*.

TABLE II

PARAMETERS ASSOCIATED WITH THE RATE LAW

$$-\frac{\mathrm{d} \ln [\mathrm{CrBr}^{2+}]}{\mathrm{d}t} = k_0 + k_{-1}[\mathrm{H}^+]^{-1}$$

$I = 1.00\ M$

	k_0	k_{-1}
$\Delta H^* \times$ mole kcal.$^{-1}$	23.8 ± 0.3	27.1 ± 0.2
$\Delta S^* \times$ mole deg. cal.$^{-1}$	-3.5 ± 0.9	4.7 ± 0.7
k (at 45°)	5.7×10^{-5} sec.$^{-1}$	1.77×10^{-5} mole l.$^{-1}$ sec.$^{-1}$

Discussion

The contrast in relative importance of transition states of charge 2+ and 1+ for aquation of bromopentaamminechromium(III) ion[7] and bromopentaaquochromium(III) ion is striking. Reaction goes to an equal extent by each of the two transition states $\{\mathrm{CrA_5Br^{2+}}\}^*$ and $\{\mathrm{CrA_4BBr^{+}}\}^*$, where A is ammonia or water and B is amide ion or hydroxide ion,[8] at a hydrogen ion concentration of $\sim 7 \times 10^{-12}\ M$ for the ammine species (at 25.3°) and 0.31 M for the aquo species (at 45°). This difference arises largely from the greater enthalpy of activation for the transition state of charge 1+ for the ammine species. For bromopentaamminechromium(III) ion $(\Delta H_{-1}^* - \Delta H_0^*)^9 = 18.2$ kcal. mole^{-1} in contrast to $(\Delta H_{-1}^* - \Delta H_0^*)^9 = 3.3$ kcal. mole^{-1} for bromopentaaquochromium(III) ion. On the other hand, values of the entropy of activation for aquation of bromopentaamminechromium(III) *via* the two pathways, $\Delta S_0^* = -6.7$ cal. mole^{-1} deg.$^{-1}$ and $\Delta S_{-1}^* = +3.0$ cal. mole^{-1} deg.$^{-1}$, are very similar to the corresponding values given in Table II for the aquo species.

There are two possible transition states of charge 1+, a conjugate base of the reactant species[10] and a combination of hydroxide ion with the reactant species. If the only important transition state of charge 1+ involved combination of hydroxide ion with the reactant species, it would be difficult to rationalize the contrasting properties of the bromoammine species and bromoaquo species just discussed. If, however, these transition states were conjugate bases of the reactants, the much greater acidity of water relative to ammonia[11] would provide a reasonable explanation for the much greater relative importance of the transition state of charge 1+ in reaction of the bromoaquo species.[12] Only for bromopentaaquochromium(III) ion does this argument demand a transition state which is a conjugate base of the reactant; for bromopentaamminechromium(III) ion the transition state could be made up of hydroxide ion and the complex ion and the argument would still be valid.[13] The similarity of values of ΔS^* for corresponding pathways for reactions of bromopentaaquochromium(III) ion and bromopentaamminechromium(III) ion suggests mildly that the transition states for analogous pathways are similar. The present data leave unanswered, however, the question of whether or not a water molecule is incorporated into these transition states.

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(7) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

(8) The specific participation of water in these transition states is not shown, but this formulation is not intended to exclude this possibility.

(9) The subscripts to ΔH^* use the notation used for rate coefficients of our rate law. For reaction of the ammine species, values of k_{-1} and ΔH_{-1}^* were obtained from values associated with the rate law term $k_\mathrm{b}[\mathrm{Cr(NH_3)_5Br^{2+}}][\mathrm{OH^-}]$ by appropriate correction using the equilibrium constant and other parameters for dissociation of water: $k_{-1} = k_\mathrm{b}K_\mathrm{w}$ and $\Delta H_{-1}^* = \Delta H_\mathrm{b}^* + \Delta H_\mathrm{w}$.

(10) F. J. Garrick, *Nature*, **139**, 507 (1937).

(11) The acidity of ammonia is discussed by R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 87-88.

(12) Y. P. Nazarenko and Y. I. Bratushko [*Ukr. Khim. Zh.*, **28**, 17 (1962); *Chem. Abstr.*, **57**, 4083g (1962)] have observed the rates of aquation of $\mathrm{Cr(NH_3)_5Cl^{2+}}$ and $\mathrm{Cr(OH_2)(NH_3)_4Cl^{2+}}$. The former rate does not increase appreciably in going from a solution with $10^{-3}\ M$ hydrogen ion to one with no added acid, but the latter rate increases by a factor of ~3 with this ill-defined change of acidity. This indicates that a rate law term $k_{-1}[\mathrm{Cr(OH_2)(NH_3)_4Cl^{2+}}][\mathrm{H^+}]^{-1}$ is neither dominant nor trivial in slightly acidic solution.

(13) Whether base hydrolysis of amminecobalt(III) species occurs by $\mathrm{S_N2}$ or $\mathrm{S_N1CB}$ mechanisms is an unsettled question. [C. K. Ingold, "Substitution at Elements Other than Carbon," Weizmann Science Press, Jerusalem, 1959, Chapter 1; M. L. Tobe, *Sci. Progr.*, **48**, No. 191, 483 (1960); F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 25 (1961).]

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Photochemical Reactions of the Difluoramino Radical with Some Inorganic Substrates

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Photolytic decomposition of the difluoramino free radical ($\mathrm{NF_2}$), present as a result of the equilibrium[1]

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(1) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960); F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

Table I

Photochemical Reactions of NF_2

Substrate	Molar ratio N_2F_4: substrate	Time, min.	Significant product	Yield, %	Process
(1) SO_2	1	149	FSO_2NF_2	89	Fluorination and difluoramination[a]
(2) SO_3	1	20	FSO_3NF_2	55	Fluorination and difluoramination
(3) POF_3	1	35	$\overset{+}{N}O\overset{-}{P}F_6$	50	Fluorination, difluoramination, and rearrangement
(4) SOF_2	2	30	SOF_4	20	Fluorination
(5) SOF_4	1	60	...	..	No reaction

[a] Reference 2.

$N_2F_4 = 2NF_2$, has been described previously and a scheme proposed to account for the photochemically-induced reaction of NF_2 with SO_2.[2] The latter undergoes fluorination and difluoramination to give FSO_2NF_2.[2] To extend the scope of this reaction to other substrates the difluoramine radical was irradiated at 2537 Å. in the presence of each of the inorganic compounds SO_3, POF_3, SOF_2, and SOF_4.

Experimental

The photochemical apparatus used in this investigation was a Pyrex vessel with an internally-sealed cold cathode mercury resonance lamp, whose principal radiation was at 2537 Å. The significant products, exposure time, yield, molar ratio of reactants, and processes are summarized in Table I.

N,N-Difluorohydroxylamine-O-fluorosulfate (FSO_3NF_2)[3] and SOF_4[4] were identified by their infrared and mass spectra. In addition, FSO_3NF_2 was characterized by its molecular weight from vapor density measurement (calcd. 151.1, found 149.3). The solid product from treatment of POF_3 with excited NF_2 is believed to be nitrosonium hexafluorophosphate ($\overset{+}{N}O\overset{-}{P}F_6$) on the basis of elemental analyses (*Anal.* Calcd.: F, 65.1. Found: F, 63.9), the infrared spectrum (a very strong broad band centering at 855 cm.$^{-1}$ and a weak one at 2379 cm.$^{-1}$),[5,6] and behavior with aziridine. This reaction evolved N_2O and ethylene, products characteristic of the action of nitrosating agents on the small ring heterocyclic amine.[7]

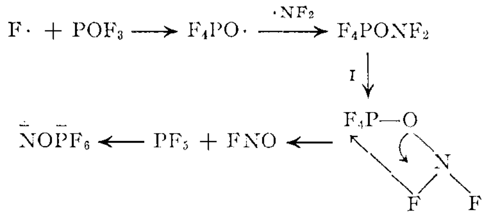
Other products from these reactions consisted of SOF_2, SO_2F_2, and N_2O from (1); SO_2F_2 and N_2O from (2); N_2O from (3); and SO_2F_2, SF_4, and SF_6 from (4). Also NF_3, NO, N_2F_2, N_2, and SiF_4, which are the photochemical decomposition products of N_2F_4 in Pyrex, were observed.

Discussion

Formation of FSO_3NF_2 from NF_2 and SO_3 parallels the production of FSO_2NF_2 from NF_2 and SO_2.[2] That is, fluorination and difluoramination occur.[8]

$$F\cdot + SO_3 \longrightarrow FSO_3\cdot \xrightarrow{\cdot NF_2} FSO_3NF_2$$

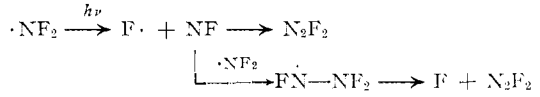
This same sequence may be applied in the case of POF_3.



Compound I, resulting from fluorination and difluoramination, does not appear stable and probably undergoes intramolecular rearrangement to give FNO and PF_5, which combine to yield the salt isolated. The alternative of a direct migration of the two fluorine atoms to phosphorous cannot be ruled out.

In contrast to the above examples, only the first step, fluorination, is observed in the reaction of NF_2 with SOF_2. The product, SOF_4, is stable under the conditions, as shown by the last entry in Table I.

Depending on the nature of the substrate, therefore, the over-all process varies widely. However, the initial step in all cases is likely the decomposition of NF_2 as previously suggested.[2] Coupling of the NF group or



reaction with NF_2 provides a reasonable route[9] to N_2F_2, which is generally a major primary product.

Since SO_3 does not absorb in the region of the spectrum employed, the energy in this case (and probably in the remaining ones in Table I) must be injected into the system *via* NF_2. The above equation readily accommodates this fact.[10]

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(2) C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, **2**, 662 (1963).

(3) M. Lustig and G. H. Cady, *ibid.*, **2**, 388 (1963).

(4) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).

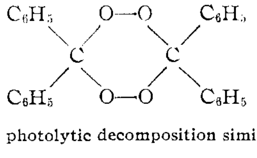
(5) D. Cook, S. J. Kuhn, and G. A. Clark, *J. Chem. Phys.*, **33**, 1669 (1960).

(6) D. W. A. Sharp and J. Thorley, *J. Chem. Soc.*, 3558 (1963).

(7) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 4417 (1961).

(8) Compare the photolytic reaction of OF_2 with SO_3: R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Angew. Chem. Intern. Ed. Engl.*, **2**, 149 (1963).

(9) Compare the reaction of $(C_6H_5)_2C$ with O_2 to give



(10) NO_2 undergoes photolytic decomposition similar to that proposed for NF_2.

$$NO_2 \xrightarrow{3130\ \text{Å.}} NO + O$$

F. E. Blacet, T. C. Holland, and P. A. Leighton, *J. Am. Chem. Soc.*, **84** 4011 (1962).