(NF_2^+, O_2NNF_2) was meaningless due to the presence of small amounts of N_2F_4 and/or NF_2 resulting from the slight decomposition of O_2NNF_2 even at about −130°. Since the vapor pressure of NO_2 is exceedingly low at −130°, any NO_2 produced by the decomposition of O_2NNF_2 would be immediately condensed in the mass spectrometer inlet system before being detected.

Discussion

The possibility that the spectrum assigned here as the new compound O_2NNF_2 could be due instead to a mixture of previously known compounds may be ruled out in the following manner. The compound $ONNF_2$ cannot be contributing to the spectrum since $ONNF_2$ is a purple solid which is pumped away below −140° whereas the substance in question is a white solid at −130 to −135°. The peak at NO_2^+ cannot be arising from NO_2F or NO_3F since there are no additional peaks at NO_2F^+ or OF^+. Furthermore, the NO_2^+ peak cannot be arising from either NO_2 or N_2O_3, since from blank experiments the vapor pressures of these compounds are exceedingly low at −130°. The fact that the spectrum in question cannot be attributed to known compounds and the fact that it uniformly increased with increasing temperature and uniformily decreased when the substance was pumped away prove that the spectrum is due to a new compound. Since the preparation of this compound involved the combination of NO_2 and NF_2 radicals, since the mass spectrum suggests that the structure contains NO_2 and NF_2 groups, since the synthesis of the related compound $ONNF_2$ was successfully duplicated and the compound was characterized, and since a stable electronic configuration for O_2NNF_2 is possible,[1b] it was concluded that this new compound was very likely nitrodifluoramine, O_2NNF_2.

The heats of formation of ONF, NO_2F, and $ONNF_2$ derived from the appearance potential data are lower than earlier values suggesting possible excess energy in the ion processes. However, some of the necessary thermodynamic values are not universally accepted. In particular, much controversy has arisen over the values for the heat of formation of OF and the ionization potential of NO_2.

A recent critical discussion of the dissociation energies D(FO–F) and D(O–F) concluded that the most likely value for D(FO–F) was 1.7 ± 0.2 eV which implied D(O–F) = 2.2 ± 0.2 eV. Recalculating D(O–F) using the revised but still controversial value of ΔH_f(F) = 0.69[11,17] eV, D(FO–F) = 1.7 ± 0.2 eV leads to $\Delta H_f(\text{OF}) = D(\text{FO–F}) + \Delta H_f(\text{OF}_2) - \Delta H_f(\text{F}) = 1.7 + 0.25^{19} - 0.69 = 1.26 \pm 0.2$ eV and $D(\text{O–F}) = \Delta H_f(\text{O}) + \Delta H_f(\text{F}) - \Delta H_f(\text{OF}) = 2.58 + 0.69 - 1.26 = 2.01 \pm 0.2$ eV. With no evidence of excess energy occurring in the appearance potential of NO_2^+ from NO_3F, our newly derived value of ΔH_f(OF) = 1.4 ± 0.1 eV is well within experimental uncertainties and seems reasonably well founded. If some excess energy is produced in process 4 of Table II, the derived value of ΔH_f(OF) would be lowered from 1.40 eV accordingly.

The most reliable determinations of $I(NO_2)$ appear to fall into two groups:[10] those centered around 10.0 eV, which may be attributed to the adiabatic ionization potential, and those centered around 11.0 eV, which may correspond to the vertical ionization potential. The large difference between the adiabatic and vertical values is caused by the NO_2 molecule being bent while the NO_2^+ ion is linear. We determined the electron impact value of $I(NO_2)$ = 11.0 ± 0.15 eV from nine independent measurements, and we have used this value in calculations in this work.

The derived heats of formation of $ONNF_2$ and O_2NNF_2 yield respective N–N dissociation energies of $D(\text{ON–NF}_2)$ = 0.82 eV and $D(\text{O}_2\text{N–NF}_2)$ = 0.71 eV which correspond favorably with $D(\text{F}_2\text{N–NF}_2)$ = 0.96 eV, $D(\text{O}_2\text{N–NO}_2)$ = 0.59 eV, and $D(\text{O}_2\text{N–NO})$ = 0.42 eV.

In summary, this work has demonstrated that the mass spectrometer is a useful tool in studying the synthesis and molecular energetics of nitrogen–oxygen–fluorine compounds. In particular, the cryogenic inlet system used here was shown to be essential for the identification and characterization of the unstable compounds nitrosodifluoramine ($ONNF_2$) and nitrodifluoramine (O_2NNF_2).

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Preparation and Reaction of Allylamine–Rhodium(III) Chloride Complexes

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Allylamine may coordinate with an olefinic double bond and an amino group serving as a bidentate ligand. In the case of allylamine complexes of copper(I)[1] and platinum(II),[2-4] such a bidentate coordination has been reported. However, the reaction of coordinated allylamine has not been reported. In this paper we report the preparation of allylamine complexes of rhodium(III) chloride and their reaction in ethanol solution.

Experimental Section

The infrared spectra were obtained with Japan Spectroscopic Models 102 and 103 spectrometers. The samples were prepared as Nujol mulls or KBr pellets. Glpc analyses were carried out with an Ohkura gas chromatograph, a 3-m Carbowax 20M on Diasolid A column at 70°, and a nitrogen flow rate of 50 cm³/min.

Preparation of Complexes. (a) $\mathbf{RhCl_3(C_3H_5NH_2)(H_2O)}$.—Allylamine (75 μl, 1 mmol) was added to a solution of rhodium trichloride trihydrate (264 mg, 1 mmol) in 10 ml of ethanol with stirring by magnetic stirrer. The reaction mixture turned to a light red from a deep red and a reddish brown precipitate appeared. After stirring for several minutes, the precipitate was filtered, washed with ether, and dried under reduced pressure.

(b) $\mathbf{RhCl_3(C_3H_5NH_2)_2}$.—Bis(allylamine)rhodium(III) chloride was synthesized by the same method as that for $RhCl_3(C_3H_5NH_2)(H_2O)$. One hundred and fifty microliters of allylamine (2 mmol) was added in this case.

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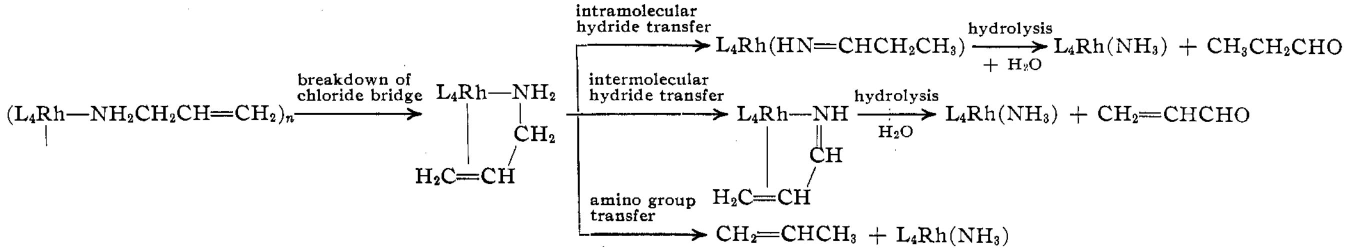
TABLE I

ALLYLAMINE–RHODIUM(III) CHLORIDE COMPLEXES AND *n*-PROPYLAMINE–RHODIUM(III) CHLORIDE COMPLEXES

Complex	Yield, %	Color	Mp (dec), °C	Ir $\nu_{C=C}$, cm^{-1}	Analytical data, % Calcd C	 H	 N	 Cl	 Found C	 H	 N	 Cl
$RhCl_3(C_3H_5NH_2)(H_2O)$	61	Reddish brown	120	1648	12.62	3.16	4.92	37.4	12.68	3.32	4.82	36.6
$RhCl_3(C_3H_5NH_2)_2$	63	Light brown	175	1648	22.3	4.4	8.7	31.8	21.53	4.39	8.50	31.4
$RhCl_3(C_3H_5NH_2)_3$	53	Orange-yellow	180	1648	28.4	5.51	11.0		28.72	5.61	11.07	
$[RhCl(C_3H_5NH_2)_5]Cl_2$	58	Yellow	170	1648	36.18	7.07	15.21		36.24	7.09	14.94	
$RhCl_3(n\text{-}C_3H_7NH_2)(H_2O)$	38	Reddish brown	155		12.6	3.8	4.9		12.77	4.09	4.66	
$RhCl_3(n\text{-}C_3H_7NH_2)_2$	44	Light brown	180		22.0	5.5	8.5		21.46	5.27	8.22	
$RhCl_3(n\text{-}C_3H_7NH_2)_3$	30	Orange-yellow	200		27.9	7.0	10.8		27.26	7.03	10.66	
$[RhCl(n\text{-}C_3H_7NH_2)_5]Cl_2$	33	Yellow	180		35.5	8.9	13.7		34.91	8.87	13.65	

SCHEME I[a]



[a] L = Cl, H_2O or allylamine.

(c) $RhCl_3(C_3H_5NH_2)_3$.—The preparation of tris(allylamine)rhodium(III) chloride was similar to that of $RhCl_3(C_3H_5NH_2)(H_2O)$. Three hundred microliters of allylamine (4 mmol) was added to a 10-ml solution of rhodium trichloride (1 mmol) in ethanol. After removal of 5 ml of solvent from the reaction mixture by evaporation under reduced pressure, 30 ml of ether was added. The resulting orange-yellow precipitate was filtered, recrystallized from methanol, washed with ether, and dried under reduced pressure.

(d) $[RhCl(C_3H_5NH_2)_5]Cl_2$.—Six hundred microliters of allylamine (8 mmol) was added to a 10-ml solution of rhodium trichloride (1 mmol) in ethanol. The resulting light yellow solution was concentrated under reduced pressure to half-volume. The cream yellow product was filtered, recrystallized from methanol, washed with ether, and dried under reduced pressure.

Yield data, melting points, infrared spectra, and elemental analyses for these allylamine complexes are summarized in Table I, together with the data for the corresponding *n*-propylamine complexes of rhodium(III) chloride which were prepared by the same procedures as for the allylamine complexes.

Reaction of Bis(allylamine)rhodium(III) Chloride in Ethanol.—After preparing bis(allylamine)rhodium(III) chloride from rhodium trichloride trihydrate (264 mg, 1 mmol) and allylamine (150 μl, 2 mmol) in ethanol (20 ml), the mixture was heated at 50° for 5 hr with stirring by a magnetic stirrer. Reaction products were analyzed by glpc, and retention times were compared with those of authentic samples. Yield data were obtained by glpc using toluene or ethylbenzene as an internal standard.

Fifty milliliters of ether was added to the reaction mixture to separate the light brown precipitate which was filtered, washed with ether, and dried under reduced pressure (mp 90–95° dec, yield 164 mg). Infrared spectrum [Nujol mull (in cm^{-1})]: 1410 (CH_2), 1580 (NH_2), 1630 (NH_3), 1720 (CO), 3200 (NH).

Reactions of other allylamine complexes of rhodium chloride in ethanol were carried out by a similar procedure and reaction products were analyzed by glpc. The reaction of $RhCl_3(C_3H_5NH_2)_3$ in the presence of hydrochloric acid ($[HCl]/[Rh(III)] = 0.5$) was also examined.

Results and Discussion

Allylamine Complexes.—The ir spectra of allylamine complexes of rhodium(III) chloride (Table I) show that allylamine coordinates to rhodium(III) with the amino group but not with the double bond. A shift of the C=C stretching band was not observed. In the case of $RhCl_3(C_3H_5NH_2)(H_2O)$ and $RhCl_3(C_3H_5NH_2)_2$, chloride may act as a bridging ligand forming a polymeric structure. The fact that these two complexes are insoluble in organic solvents suggests the polymeric structure. Generally, the coordination of an olefinic double bond to rhodium(III) is difficult.[5] The coordination of an olefin to rhodium(III) at low temperatures is reported by nmr studies,[6] but the isolation of an olefin–rhodium(III) complex is reported only in case of arylfulvene.[7] The four kinds of allylamine complexes resemble the corresponding *n*-propylamine complexes in their color and solubility.

Thermal Decomposition Reaction of Allylamine Complexes in Ethanol Solution.—The results of the reaction of allylamine complexes of rhodium(III) chloride in ethanol solution are shown in Table II. In the cases of $RhCl_3(C_3H_5NH_2)(H_2O)$ and $RhCl_3(C_3H_5NH_2)_2$, the reaction occurred at 50° and the formations of *N*-propylideneallylamine, acrolein, propionaldehyde, propylene, and three unidentified materials were confirmed by glpc. The complexes $RhCl_3(C_3H_5NH_2)_3$ and $[RhCl(C_3H_5NH_2)_5]Cl_2$ were stable and no reaction occurred even with refluxing. Tris(allylamine)rhodium(III) chloride, however, is found to react at 50° in the presence of hydrochloric acid. Figure 1 shows the ir spectra of the complex obtained from the reaction

TABLE II

REACTION OF ALLYLAMINE–RHODIUM(III) CHLORIDE COMPLEXES

Complex	Temp, °C	Yield,[a] mol % based on allylamide (1)	 (2) + (3)	 (4)	 (5)	 (6)	 (7)
$RhCl_3(C_3H_5NH_2)(H_2O)$	50	74	2	0	3.5	0.5	6
$RhCl_3(C_3H_5NH_2)_2$	50	13	2	0.1	1	1.5	1.5
$RhCl_3(C_3H_5NH_2)_3$	78	No reaction					
$RhCl_3(C_3H_5NH_2)_3$[b]	50	3.5	2.5	0.1	0.5	1	2
$[RhCl(C_3H_5NH_2)_5]Cl_2$	78	No reaction					

[a] (1) $CH_3CH_2CH=NCH_2CH=CH_2$; (2) CH_3CH_2CHO; (3) $CH_2=CHCHO$; (4) $CH_2=CHCH_3$; (5)–(7) unidentified. [b] HCl was added ($[HCl]/[Rh(III)] = 0.5$); time, 5 hr.

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of $RhCl_3(C_3H_5NH_2)_2$ in ethanol at 50°. The bands at 930 cm^{-1} (δ_{CH}), 990 cm^{-1} (δ_{CH}), and 1648 cm^{-1} ($\nu_{C=C}$) decreased with the reaction time, and the carbonyl stretching band (ν_{CO} 1720 cm^{-1}) appeared. This suggests that a carbonyl compound which is derived from allylamine coordinates to rhodium(III). The bands at 1630 and 3200 cm^{-1} indicate the coordinated ammonia. This compound is insoluble in solvents and further characterization was unsuccessful.

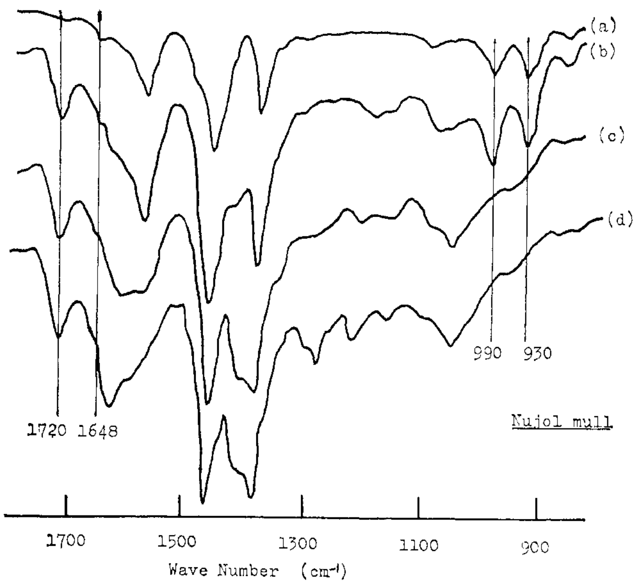

Figure 1.—Infrared spectra of the reaction product from bis(allylamine)rhodium(III) chloride at 50° in ethanol. Reaction time: (a) zero, (b) 10 min, (c) 30 min, (d) 60 min.

The coordination of the double bond to rhodium(III) in an intermediate state may be necessary for the reaction of coordinated allylamine. In the complexes $RhCl_3(C_3H_5NH_2)(H_2O)$ and $RhCl_3(C_3H_5NH_2)_2$, the coordination of the double bond to rhodium(III) after the breakdown of the bridging of chloride ion is considered to occur in an intermediate state. After π-complex formation, hydride transfer and amino group transfer occur. A hydride-transfer reaction with subsequent hydrolysis gives acrolein and propionaldehyde. An amino group transfer reaction causes the formation of propylene (Scheme I). In case of the rearrangement of allyl alcohol catalyzed by rhodium trichloride, a similar hydride transfer and hydroxide transfer have been reported.[8,9] *N*-Propylideneallylamine is obtained from propionaldehyde and allylamine.[10]

The complexes $RhCl_3(C_3H_5NH_2)_3$ and $[RhCl(C_3H_5NH_2)_5]Cl_2$, in which chloride ion and amino groups occupy all of the coordination sites and prevent the double bond from coordination, do not react under the above conditions. However, hydrochloric acid reacts with coordinated allylamine to give allylammonium ion and the coordination of the double bond becomes possible in an intermediate state and reaction occurs

$$L_5RhNH_2CH_2CH{=}CH_2 \xrightarrow{+H^+} L_5Rh(CH_2{=}CHCH_2NH_3^+) \rightsquigarrow \text{propionaldehyde, acrolein, propylene}$$
$$(L = Cl \text{ and allylamine})$$

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On the Existence of Binuclear Aquocobalt(III) Perchlorates. Oxygen-18 Studies

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Several lines of conflicting evidence appear in the literature concerning the species present in acidic aqueous cobalt(III) perchlorate solutions. The main questions are as follows. (a) What is the value of the first hydrolysis constant ($\sim 10^{-3}$ or 10^{-1})? (b) What is the thermodynamic stability and the composition of binuclear, hydroxy-bridged species? (c) What is the magnitude of the velocity of reaction relating these ions?

A recent review[1] summarized the lines of evidence on these topics. The strongest evidence for the existence of di-μ-hydroxy-bridged cobalt(III) dimers in 1–6 *M* $HClO_4$ comes from ^{18}O experiments[2] where the molecular oxygen derived from the oxidation of water by Co^{3+} apparently comes partially from the inner, nonsolvent-equilibrated coordination sphere of the metal ion. In the initial part of the reaction it approaches 50% and overall comprises about 6% of the oxygen contained. It is known, however, that the Co^{2+}–Co^{3+} electron exchange is rapid,[3] that the Co^{2+} water exchange is very rapid,[4] and that Co^{3+} solutions invariably contain significant quantities of Co^{2+}.[4,5]

Thus, one expects the apparent water-exchange rate to be rapid, faster than the relatively slow rate of water oxidation under the usual concentration conditions. An early study[4] of the water-exchange rate of $Co(H_2O)_6^{3+}$ showed complete exchange in about 2 min at 0°. However, only *ca.* 50% of the cobalt was in the higher oxidation state and, as was pointed out, the presence of Co^{2+} would be expected to increase the apparent rate. It is significant, however, that no oxygen holdback was observed in this study.

The explanation of the ^{18}O data[2] from the oxidation of water by Co(III) assumed the presence of di-μ-hydroxy-bridged species in which the OH groups are relatively nonlabile, that K_{eq} for the formation of the bridged species from the hydroxy monomer is large, and that molecular oxygen is derived from the bridging groups. Further it was suggested on the basis of the nonstatistical distribution of ^{18}O in the molecular oxygen that both oxygens came from the same ion.

While qualitatively consistent with several types of data, the suggestion that appreciable concentrations of dimers exist in 0.6 *M* Co^{3+} and 6 *M* $HClO_4$ requires an abnormally large K_{eq} of hydrolysis and/or a very favorable dimerization constant. Evidence has been mounting that these dimers do not have such a high thermodynamic stability.[6] However, the isotopic experiments, if correct, are so definitive that they cannot

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