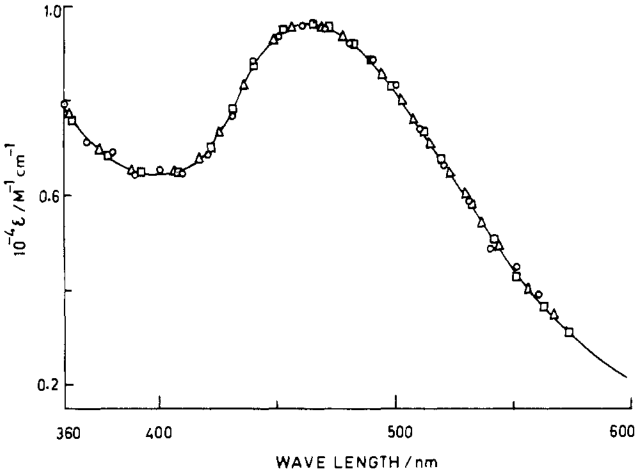

Figure 1. Visible spectra of the Ni(IV) complex in the absence and the presence of nucleophiles (X): line, Ni(IV) complex (1×10^{-4} M); point, mixture containing $[\mathrm{Ni(IV)}]_0 = 1 \times 10^{-4}$ M, and $[X] = 1 \times 10^{-3}$ M; circle, azide; triangle, thiocyanate; square, cyanide; spectra were run in aqueous media with $\mu = 0.25$ M, $T = 35$ °C, pH 7, and the time scale in a 50-ms mode.

monia (each in concentration range $(1-50) \times 10^{-3}$ M), pyridine, glycine, imidazole, L-histidine, nitrilotriacetate, ethylenediaminetetraacetate, 2,2′-bipyridine, and 1,10-phenanthroline (each in the range $(1-10) \times 10^{-3}$ M). Kinetic data are available as supplementary material. The k_{obsd} values were also independent of the concentration and nature of the buffer used.[2] These observations suggested that under the conditions employed, the Ni(IV) disappearance rates were independent of the extent and the nature of the nucleophile present and that they depended only on $[H^+]$ of the medium. The acid decomposition rates of Ni(IV), in the pH range 1.4–12.3, follow eq 7 in ref 2.

This decomposition process may involve either (a) a rate-determining intramolecular ligand oxidation followed by a rapid dissociation of the oxidized ligand[4,5] or (b) a rate-determining axial ring opening or dissociation preceding a rapid oxidation of the ring-opened or dissociated ligand. The latter mechanism can easily be ruled out by the spectral observations reported previously.[2]

The present observations also establish that the Ni(IV) species, $[\mathrm{Ni(dmg)_3}]^{2-}$ and $[\mathrm{Ni(dmg)_3(H)}]^-$ (which are the predominant species in the pH range employed), do *not* have a labile site available for substitution in the presence of strong nucleophiles or intermolecular electron transfer by a substitution-controlled route in the presence of oxidizable substrates such as L-ascorbic acid,[6a] NH_2OH,[6b] $N_2H_5^+$,[6c] 1-*tert*-butylhydrazinium ion,[6c] and 1-phenylhydrazinium ion.[6d] The nucleophilic substrates (X), some of which also possess good reducing properties, are not oxidized, perhaps because of low redox potential of Ni(IV) (e.g., $E([\mathrm{Ni^{IV}(dmg)_3(H)}]^-/[\mathrm{Ni^{III}(dmg)_3(H)}]^{2-}) \approx 0.4$ V).[6a,7]

Whether the two electrons involved in the intramolecular ligand oxidation are transferred concurrently or transferred in a stepwise manner[5] cannot easily be inferred. Although evidence from ESR data at low temperatures has been obtained[1,6a] for a paramagnetic Ni(III) species in the ascorbic acid reduction of Ni(IV), the moderately high substitution lability[8] and redox reactivities of most Ni(III) complexes[8,9] discount the kinetic importance of a Ni(III) species in this system. The rate-determining step of intramolecular ligand oxidation, therefore, most probably involves a concurrent two-electron transfer.

The above arguments may not, however, apply to the diprotonated "kinetic intermediate" species $[\mathrm{Ni(dmg)_3(H)H}]$ (in which the second protonation is most probably a direct proton addition to a ligand nitrogen[2]) as sufficient data are not yet available to make an unambiguous judgment.

Acknowledgment. Support from the UGC and the CSIR, New Delhi, is gratefully acknowledged.

Registry No. $[\mathrm{Ni(dmg)_3}]^{2-}$, 25973-84-6.

Supplementary Material Available: A table containing pseudo-first-order rate constants for the acid decomposition of the Ni(IV) complex (3 pages). Ordering information is given on any current masthead page.

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Formation and Structure of an Unusual Complex from the Reaction of Formaldehyde with Alkali Halide Salt Molecules in Argon Matrices

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The chemistry of formaldehyde is of interest[1,2] due to its ability to coordinate to acids through the oxygen or to undergo nucleophilic attack at the carbon. In the latter case, weak complex formation is envisioned initially,[3] although theoretical calculations suggest that strong nucleophiles such as F^- should bind very tightly.[4,5] The salt/molecule[6-9] was developed in conjunction with matrix isolation for the synthesis and characterization of anions formed through halide ion transfer; for example, the reaction[10] of CsF with CF_2O was shown to give the CF_3O^- anion paired with Cs^+ in good yield. On the basis of analogy to CF_2O, as well as on theoretical calculations, the reaction of CsF with CH_2O might well give rise to the intermediate CH_2FO^- anion. At the same time, previous studies have shown that the cesium salts of the heavier halogens do not readily form such intermediate anions.[10,11] With this

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background, a study was undertaken to characterize the anions formed through reaction of CH_2O with CsF and a variety of alkali halides.

The experiments in this study were all carried out on a matrix isolation system that has been described previously.[12] The alkali halide salt deposition was conducted as in previous studies; all alkali halide salts that could be vaporized with the current oven configuration (600 °C) were employed. CH_2O was sublimed at approximately 65 °C from solid paraformaldehyde and mixed with argon and the alkali halide during the deposition process. The majority of the spectra were recorded on a Beckman IR-12 infrared spectrophotometer; the most recent spectra were recorded on a Perkin-Elmer 983 spectrometer, with capabilities to 180 cm^{-1}. In either case, resolution was approximately 1 cm^{-1} in the regions of interest.

When CsF was codeposited with CH_2O into argon matrices, several new infrared spectral features were observed, the most intense of which was observed at 1680 cm^{-1}, with an optical density of up to 0.40 in the highest yield experiments. Additional, weaker bands at 1491 and 2845 cm^{-1} were noted near the ν_3 and ν_1 fundamentals of CH_2O. Finally, careful spectra were recorded in the low-energy region below the fundamental of CsF, and a band was noted at 264 cm^{-1}. When concentrations were increased, these product bands grew at a uniform rate, and weak, broad absorptions due to aggregates were noted in the region 1710–1725 cm^{-1}.

After these initial experiments, the following alkali halides were vaporized and codeposited with CH_2O: CsCl, CsBr, CsI, RbI, KCl, KBr, KI, NaBr, and NaI. For the last two (sodium) salts, no reaction was noted with CH_2O, while for the remaining salts, distinct new product absorptions were detected. In each case, a sharp, moderately intense product band was noted between 1688 and 1698 cm^{-1}; the alkali iodides all gave rise to a band at 1688 ±1 cm^{-1}, which appears for the alkali bromides at 1694 cm^{-1} and the alkali chlorides at 1698 cm^{-1}, in each case independent of the cation. Unfortunately, the only volatile fluoride salt (under the present experimental conditions) was CsF, as reported above, so no comparisons can be made within the alkali fluorides. Finally, in several of the highest yield experiments, bands were again noted near two of the CH_2O fundamentals,[13] ν_1, the CH_2 symmetric stretch, and ν_3, the CH_2 in-plane deformation. The positions of these weak absorptions varied just slightly (1–2 cm^{-1}) with halide anion and not at all with metal cation.

These spectra collectively indicate that a distinct product was formed during the reaction of alkali halides with CH_2O, but the product formed was *not* the expected CH_2XO^- anion. This conclusion is based on the fact that similar spectra were obtained with all of the halides employed, while previous studies have shown that fluoride behaves much differently and gives a much higher yield of halide-transfer product. In addition, no new band was noted that could be attributed to a C–X stretching mode, as would be required for a CH_2XO^- species. Thirdly, while the bands between 1680 and 1700 cm^{-1} can be readily assigned to a C–O stretch in the product, this band is only shifted some 50–60 cm^{-1} from parent CH_2O, indicating that considerable double-bond character remains. For comparison,[10] the reaction of CsF with CF_2O to yield the CF_3O^- anion caused a shift of over 400 cm^{-1} in the C–O stretching mode and gave rise to a new C–F stretch in the appropriate spectral region, while the reaction of CsCl with CF_2O did not give rise to a product species. Finally, the spectra were all indicative of a perturbed CH_2O subunit in a molecular complex, rather than a distinct new species. These observations, collectively, indicate that the product absorber is not the CH_2XO^- anion, which would be anticipated on the basis of theoretical calculations and by analogy to CF_2O.

Table I. Infrared Band Positions and Assignments for the Reaction Product of Formaldehyde with Alkali Halide Salt Molecules

alkali halide[a]	ν_1,[b] cm^{-1}	ν_2,[b] cm^{-1}	ν_3,[b] cm^{-1}	ν_{MX}, cm^{-1}
CsF	2845	1680	1491	264
CsCl		1698	1497	
CsBr	2847	1694	1495	
CsI	2848	1688	1491	
RbI	2848	1689	1491	
KI		1689	1491	
KBr		1694		
KCl		1698		
	2800[c]	1744[c]	1499[c]	

[a] No reaction was observed with either NaBr or NaI. [b] Vibrations of the CH_2O subunit: ν_1, symmetric CH_2 stretch; ν_2, carbonyl stretch; ν_3, CH_2 symmetric deformation. [c] Isolated CH_2O.

Several possible structures remain for the product species; before consideration of these, it should be noted that the complex is relatively strongly bound in that the carbonyl stretch is shifted much more in the present product species than in the hydrogen-bonded complexes[14] $CH_2O{\cdot}HX$ as is the CH_2 in-plane deformation mode. The most intense feature for all of the reactive alkali halides was the perturbed carbonyl stretch; Table I indicates no alkali-metal dependence of this mode, while a distinct halide anion dependence was noted. This rules out a structure in which the alkali metal interacts with the carbonyl oxygen, analogous to a hydrogen bond. A second possibility is a hydrogen-bonding interaction between the halide anion and one or both of the C–H bonds of CH_2O. However, such an interaction would be expected to shift the C–H stretching modes significantly to lower energy, not higher (as observed).[15] In addition, this mode of interaction should not dramatically perturb the carbonyl portion of the molecule; hence, this structure may be eliminated.

The preferred structure for this product species is one reminiscent of nucleophilic attack on the carbon by the halogen of the alkali halide, but without carbon–halogen bond formation. Rather, a dipolar or ion–dipole interaction is envisioned between the considerable negative charge on the halogen and the partial positive charge of the carbon. This would account for the significant anion dependence of the shift of the carbonyl stretch and the lack of metal dependence. The lack of formation of a carbon–halogen bond, in view of expectations and theoretical calculations, must be due to the presence of the metal cation. This point is supported by the observation of a band at 264 cm^{-1} when CsF was codeposited with CH_2O; this band can be readily assigned to the stretching mode of the perturbed CsF unit in the dipolar complex, shifted down from the parent position at 313 cm^{-1}. Of the remaining alkali halides employed, only KCl has the parent fundamental above 200 cm^{-1}; the yield in the KCl + CH_2O experiment was sufficiently low that observation of a perturbed KCl unit was not possible. The lack of reaction of NaBr and NaI with CH_2O also points up the importance of the alkali-metal cation; the low reactivity of sodium salts in such experiments has been noted previously.[16] Finally, the thermodynamic role of the cation in salt/molecule reactions has been discussed in some detail and provides a rationale for the low reactivity of sodium salts.[17]

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One remaining point is the variation of the C–O stretch with the halide; the observed order ($I^- > Br^- > Cl^-$) follows the acidity order of the halides in the hydrohalic acids, except for F^-, which showed an anomalously large shift. This suggests an additional covalent interaction with F^- not present with the heavier halogens, as might be expected from the unique chemistry of the fluoride anion. A similar order of perturbation was noted for the CH_2 symmetric stretch and the CH_2 in-plane deformation modes, the two vibrations anticipated to be perturbed most significantly by the type of interaction proposed here.

In conclusion, the codeposition and reaction of alkali halide molecules with formaldehyde in argon matrices did not give rise to the expected halide anion transfer and formation of the CH_2XO^- anion. Rather, an unusual ion–dipole interaction was indicated between the halide anion and the carbon center of CH_2O, although in the case of CsF slight indication of a covalent interaction was noted. Theoretical studies of this system, including the alkali-metal cation, would be useful to fully characterize the nature of the interaction observed here.

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Registry No. CsF, 13400-13-0; CsCl, 7647-17-8; CsBr, 7787-69-1; CsI, 7789-17-5; RbI, 7790-29-6; KI, 7681-11-0; KBr, 7758-02-3; KCl, 7447-40-7; formaldehyde, 50-00-0.

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Infrared Study of Sulfur-Containing Iron Oxide. Behavior of Sulfur during Reduction and Oxidation

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When an SO_4^{2-} ion was introduced from $(NH_4)_2SO_4$ or H_2SO_4 onto Fe_2O_3, the resulting catalysts exhibited pronounced catalytic activities for acid-catalyzed reactions such as the ring-opening isomerization of cyclopropane, the dehydration of 2-butanol, and the skeletal isomerization of *n*-butane[1-3] on the one hand and were quite effective for a coal liquefaction[4] on the other. Though the oxidation state of sulfur in the former was believed to be S^{6+} and the electrophilic property of the S═O bond accounted for the enhanced acidic properties,[2] the role and the active state of S in the latter are still unknown, since the reaction is usually carried out under a high pressure of hydrogen and at high temperature and the introduced SO_4^{2-} ion could be reduced to lower oxidation states. This report deals with the influences of the source of sulfur and of the successive treatment on the oxidation states of the sulfur introduced. IR spectroscopic investigations were performed on the iron oxide treated with H_2S, SO_2, and $(NH_4)_2SO_4$ under oxidized conditions, and XPS measurements were employed to examine the states of sulfur under reduced conditions.

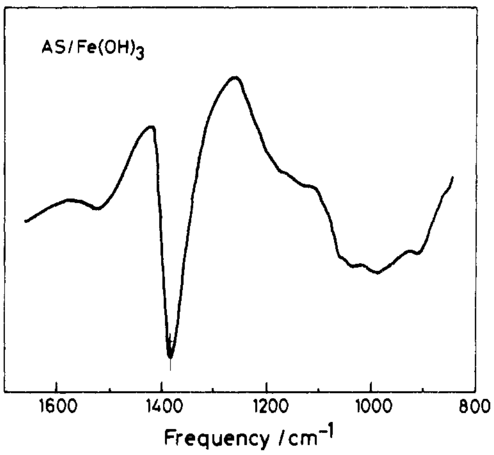

Figure 1. IR spectrum of $AS/Fe(OH)_3$ calcined at 500 °C.

Experimental Section

Iron hydroxide ($Fe(OH)_3$) was prepared by treatment of an aqueous solution of $Fe(NO_3)_3$ with aqueous ammonia (final pH 8–9), followed by washing and drying of the product at 100 °C. The sulfur-promoted catalysts were prepared by introducing inorganic sulfur compounds onto the hydroxide or the hydroxide calcined at 300 °C, followed by various treatments such as calcination, reduction, and oxidation. The $(NH_4)_2SO_4$-impregnated catalysts ($AS/Fe(OH)_3$) were prepared by immersing $Fe(OH)_3$ in an aqueous solution of ammonium sulfate, followed by calcining at 500 °C. The amount of sulfur loading was adjusted to ca. 2 wt % as SO_3. The H_2S-treated catalysts ($Fe(OH)_3$–H_2S) and SO_2-treated catalysts ($Fe(OH)_3$–SO_2) were obtained by treating $Fe(OH)_3$ with 9 torr of H_2S and SO_2 at desired temperatures. Starting materials and treating reagents are denoted as Fe_2O_3–H_2S etc.

The IR spectra of self-supported disks were recorded on a JASCO DS-701G infrared spectrometer at room temperature. Prior to the measurement, the samples were oxidized with O_2 at 350 °C for 10 min and evacuated at 350 °C, if necessary. The oxidation process was necessary to avoid low transmittance of samples.

X-ray photoelectron spectroscopy was performed on a VG ESCA 3 spectrometer. A reduction by H_2 and an oxidation by O_2 were carried out in a preparation chamber connected to the spectrometer. An H_2S treatment was performed in a separate vacuum manifold.

Results and Discussion

An $AS/Fe(OH)_3$ sample gave an intense band at 1370 cm^{-1} after evacuation above 300 °C (Figure 1). The changes of the ν_{SO} spectra from the hydrated $AS/Fe(OH)_3$ in the ν_1 and ν_3 region (900–1400 cm^{-1}) upon evacuation have been reported previously.[2] These spectra indicated a species of reduced C_{2v} symmetry with four bands (1240, 1140, 1025, and 924 cm^{-1}) arising from ν_1 and splitting of the triply degenerated ν_3 vibration. Upon evacuation, another set of absorptions appeared at 1340, 1140, 1015, and 915 cm^{-1}. The vibrations giving frequencies at 1340 and 1140 cm^{-1} are mainly associated with the free $>SO_2$ group, and the vibrations giving frequencies at 1015 and 915 cm^{-1} are mainly from the S–O vibrations of the $S(O–)_2$ group. Further evacuation above 100 °C resulted in a marked increase in intensity of the 1340-cm^{-1} band and a shift to 1370 cm^{-1}. Thus the band at 1370 cm^{-1} has been assigned to the asymmetric vibration of S═O bonds of the $O_2S(O–)_2$ species.[2] This assignment is supported by the spectra of organic covalent sulfates[5] (RSO_2R), which show absorption

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