

Figure 1. Fourier-transform (22.6 MHz) ^{13}C NMR spectra of $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ in THF-d_8 , -80°C .

A single temperature-invariant peak at τ 29.26 is observed for **2a** in THF-d_8 in the ^1H NMR spectrum. Its ^{13}C NMR (22.6 MHz) spectrum provides evidence for a carbonyl bridged system in a structure of apparent C_s symmetry at the slow exchange limit (Figure 1). At -80°C , eight resonances of 1:2:2:1:2:1:1:2 intensity are observed in the $^{13}\text{C}\{^1\text{H}\}$ spectrum at δ 281.1, 280.9, 205.3, 205.1, 203.3, 200.3, 200.0, and 199.0, respectively. The resonances at δ 281.1 and 280.9 are by far the lowest field carbonyl resonances yet observed for a ruthenium species and are clearly assignable to bridging carbonyls (aa', b). Of the upfield resonances, only those at δ 205.1 and 200.3 remain relatively unaffected by proton coupling. These are assigned to carbonyls d and f, respectively, since they are farthest removed from the two edge-bridging hydrogens. Carbonyls ee' and gg' are expected to couple most strongly to the trans hydrogens and are thus assigned to the resonances at δ 203.3 ($J = 10.3$ Hz) and 199.0 ($J = 5.9$ Hz), respectively.

Variable-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure 2) of **2a** facilitated the shift assignments. At -50°C , the four lowest field resonances have noticeably broadened and attenuated with respect to the four highest field resonances. At -30°C , the high-field peaks have also begun to broaden, while the low-field peaks have collapsed into the baseline. At 60°C , one resonance is observed at the weighted average of the low-temperature shifts.

We account for the spectra in Figure 2 in the following way. Commencing at about -50°C , a selective, cyclic exchange occurs around the Ru_3 basal plane involving only the bridging carbonyls (aa', b) and basal equatorial carbonyls (cc', d).⁹ Such exchange would occur through an unbridged intermediate which is forced to re-form carbonyl bridges about the same cluster face owing to occupation of two of the remaining three tetrahedral edges by bridging hydrogens. Complete exchange averaging occurs at higher temperatures and no unique mechanism is extractable from the data. It is entirely possible that a combination of exchange mechanisms is operative above 0°C . Intranuclear CO and H exchange or intranuclear H exchange coupled with localized axial-equatorial carbonyl exchange about each ruthenium vertex are reasonable routes to the averaging of ligand environments.

Variable-temperature ^{13}C NMR spectra of **1** (not described in detail here) are consistent with the interpretation⁴ of Koepke, Johnson, Knox, and Kaesz of the variable-temperature ^1H NMR spectra of $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$. The presence of two isomers is indicated below -80°C (one of C_{3v} symmetry and the other of C_2 or C_{2v} symmetry) which rapidly interconvert at room temperature. The ^{13}C NMR spectra give no evidence for bridging carbonyls at any of the temperatures observed (-127 to $+27^\circ\text{C}$). Four ^{13}C resonances are observed for **1** at -90°C (δ 201.4, 199.3, 196.5, 193.3). At $+27^\circ\text{C}$, only one sharp peak is seen at δ 198.2. The exchange mechanism is

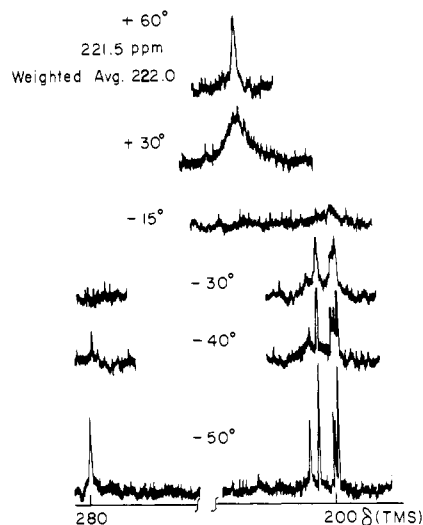


Figure 2. Variable-temperature ^{13}C NMR spectra of $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ in THF-d_8 .

presumed to occur through intramolecular hydrogen exchange coupled with localized axial-equatorial carbonyl exchange about each ruthenium vertex.

We plan to test the general applicability of this method for selectively generating in high yield cluster anions from their conjugate cluster acids.

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Matrix Infrared Spectrum of the O_2Br Radical. Bonding in the O_2X Species

Sir:

Recently, a number of fluorine- and chlorine-atom matrix reactions with nonmetal oxides have been investigated in this laboratory.¹⁻⁵ During the course of several of these studies, the previously identified dioxygenyl radicals, O_2F^{6-8} and O_2Cl ,⁹ had been observed as secondary reaction products. We have recently extended these investigations to include the corresponding matrix reactions of atomic bromine. However, at the time of this writing, the analogous O_2Br radical had not yet been identified. Consequently, in an attempt to prepare and

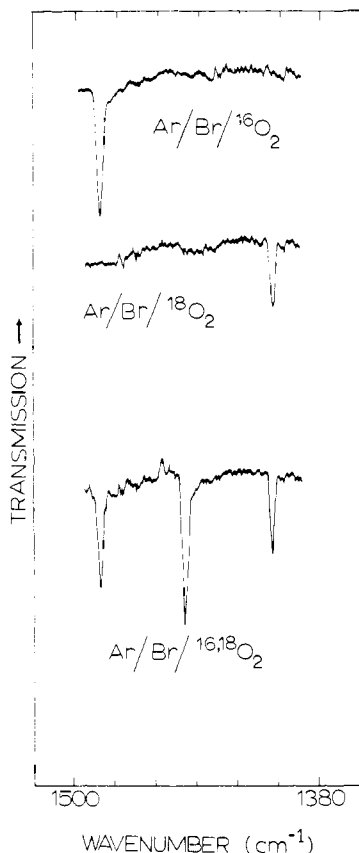


Figure 1. High resolution infrared spectra (1380–1500 cm^{-1}) of codeposited Ar/Br₂ (discharged) + Ar/O₂ matrix samples at 10 K. Top trace depicts a 200:2:1 Ar/Br/¹⁶O₂ sample, while the middle spectrum shows a 400:4:1 Ar/Br/¹⁸O₂ sample (99.4% ¹⁸O) and the lower trace corresponds to a scrambled oxygen isotopic 100:1:1 Ar/Br/^{16,18}O₂ sample (45% ¹⁸O).

identify this species, we report herein the results of a detailed infrared spectroscopic examination of the matrix reactions of bromine atoms with O₂ molecules as provided by the simultaneous condensation of Br + O₂ in argon matrices onto a 10 K infrared-transmitting window. Subsequent experiments were conducted with oxygen-18 labeled O₂ in an effort to characterize the primary reaction products.

The experimental techniques have been described in detail in an earlier publication.⁴ Bromine atoms were generated by passing a dilute mixture of Br₂ in argon (Ar/Br₂ = 200) through a low-power (70 W) microwave cavity (2.45 GHz) which was subsequently cocondensed with a separate matrix sample of molecular oxygen (Ar/O₂ = 100) onto a 10 K CsI window. The infrared spectrum of the final deposit contained a single new absorption at 1487.0 cm^{-1} which was not present in either a discharged Ar/Br₂ matrix deposit or an Ar/O₂ sample, taken separately. Other than a broad, weak feature of aggregated bromine near 313 cm^{-1} , no lower frequency absorptions were observed even under conditions where the optical density (OD) of the 1487.0- cm^{-1} band was >1.0.

When an argon matrix sample of oxygen-18 enriched O₂ (99.4% ¹⁸O) was deposited with bromine atoms, the 1487.0- cm^{-1} absorption was displaced to 1403.0 cm^{-1} . Simultaneous deposition of a scrambled 45% oxygen-18-enriched oxygen matrix sample with a discharged argon-bromine mixture produced three new infrared features at 1486.8 (optical density = 0.145), 1445.7 (OD = 0.23) and 1402.8 (OD = 0.10) cm^{-1} with observed bandwidths at half-intensity of 2.0, 2.3, and 1.8 cm^{-1} , respectively. The high resolution spectra are displayed in Figure 1 and the frequencies contained in Table I.

The assignment of the 1487.0- cm^{-1} absorption to ν_1 , the

Table I. Frequencies^a Observed for the Oxygen-Oxygen Stretching Vibration of Oxygen Isotopic O₂Br Radicals in Solid Argon at 10 K

¹⁶ O ₂ + Br	^{16,18} O ₂ + Br	¹⁸ O ₂ + Br	Assignment
1487.0	1486.8		¹⁶ O ¹⁶ OBr
	1445.7		¹⁶ O ¹⁸ OBr, ¹⁸ O ¹⁶ OBr
	1402.8	1403.0	¹⁸ O ¹⁸ OBr

^a In reciprocal centimeters.

Table II. Oxygen-Oxygen Stretching Frequencies of Several Known O₂X Compounds and the Dissociation Energies of the Corresponding OX Compounds

O ₂ X	D _e (O-X), ^a kcal/mol	ν (O-O), cm^{-1}	Ref
O ₂ F	37 ± 3	1494	6, 7, 8
O ₂ Cl	64 ± 1	1441	9
O ₂ Br	55.3 ± 0.1	1487	This work
O ₂ H	101.3 ± 0.5	1102	11, 12, 13

^a B. deB. Darwent, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **31**, 1-48 (1970).

O-O stretching vibration, of an O₂Br radical is straightforward. Its oxygen-18-isotopic frequency shift (84.0 cm^{-1}) agrees with that calculated on the basis of an O-O diatomic oscillator (85.0 cm^{-1}), while its magnitude is in the same general vicinity as the corresponding O-O stretching vibration of O₂F (1494 cm^{-1})⁶ and O₂Cl (1441 cm^{-1}).⁹ Our apparent inability to resolve the splitting of the isotopic triplet in the scrambled ¹⁶O,¹⁸O-experiment suggests that the oxygen atoms in O₂Br are equivalent. However, in the analogous O₂F species (a bent O-O-F radical), this same feature was unresolved, while, in the O₂Cl case, it was barely resolved with a 2.2- cm^{-1} splitting.⁹ In the present case, a slight broadening of this central isotopic component suggests the presence of two overlapping bands and hence inequivalent oxygen atoms. An examination of the oxygen-isotopic components of the two lower frequency vibrations of O₂Br might have resolved this dilemma. Unfortunately, because of either their inherently weak infrared intensity or their occurrence below our detectability limit (~200 cm^{-1}), they were not observed.

The frequency observed for ν_1 of O₂Br is somewhat higher than expected on the basis of the [p(s)- π^*] σ bonding model of Spratley and Pimentel.¹⁰ According to that model, the oxygen-oxygen bond strength and hence the O-O stretching frequency in O₂X compounds should decrease with decreasing electronegativity of the X group. This trend is shown to hold for fluorine (1494 cm^{-1}),⁶⁻⁸ chlorine (1441 cm^{-1}),⁹ and hydrogen (1102 cm^{-1}),¹¹⁻¹³ but not bromine (1487 cm^{-1}). This apparent anomaly in the O₂X series may be rationalized by modifying the Spratley-Pimentel model to include consideration of the X-O bond strength. A weak X-O bond would tend to favor a higher O-O stretching frequency since less of the p (or s) electron of X would overlap the antibonding π^* orbital of O₂ to form the new [p(s)- π^*] σ bond.

Fluorine is known to commonly form weaker than expected bonds (by ~26 kcal/mol) based on extrapolation using the other three halogens. An excellent discussion of this phenomenon has been presented by Politzer¹⁴⁻¹⁶ who suggests that this behavior may arise as a result of the unusually high repulsive forces an approaching electron feels from the electrons already associated with the fluorine atom. Applying this reasoning to the O₂F compound, a weakened O-F bond would tend to favor a higher than expected ν_1 frequency. In the O₂Cl compound, the O-Cl bond is expected to be stronger than the O-F bond which should result in a decreased ν_1 frequency as observed (1494 → 1441 cm^{-1}). Going on still further to the

O₂Br case, the strength of the O-Br bond is expected to be less than that of O-Cl, which results in the observed increase in the ν_1 frequency (1441 \rightarrow 1487 cm⁻¹). Interestingly enough, this trend in the ν_1 frequencies of the O₂X species (X = H, F, Cl, Br) parallels the reverse trend in the bond dissociation energies of the O-X radical molecules (Table II). It would thus appear that factors other than electronegativity must be included in any bonding scheme involving the X-O₂ or related X-NO moieties. Furthermore, in any such bonding scheme, the rather unique properties of fluorine must be taken into consideration.

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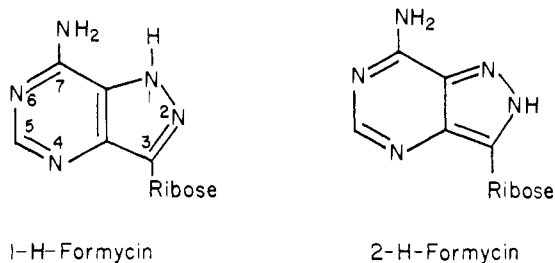
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Dynamics of Tautomerization of Formycin

Sir:

Both experimental and theoretical investigations have shown that formycin A (7-amino-3 β -D-ribofuranosyl-1H-pyrazolo[4,3-d]pyrimidine), an important analogue of adenosine, undergoes a temperature-dependent tautomeric equilibrium between N(1) H and N(2) H forms.¹⁻⁵ Some of these



studies suggest that the N(1) H tautomer is dominant, although under some conditions the N(2) H form can be detected in amounts of 15% or so.⁵ Above the formycin absorption maximum of 295 nm, the two tautomers have different extinction coefficients, with the N(2) H tautomer having the greater absorbance.^{1,6} This situation makes it possible to study the temperature-dependent tautomerization by absorbance measurements. In addition, it opens the possibility for exploring the dynamics of tautomerization by temperature-jump relaxation methods, with an optical detection system.

We found that, although in buffered solutions (e.g., 2 mM imidazole, pH 7) the absorbance changes are too rapid ($\tau < 10^{-5}$ s) to follow by our temperature-jump system,⁷ in unbuffered solutions (e.g., 0.1 M NaCl, pH 5-7) a single relaxation process is easily detected with a time constant of $\sim 10^{-4}$ s at 25 °C. The relaxation time is concentration independent over the range of 10^{-5} to 10^{-3} M. This verifies that a unimo-

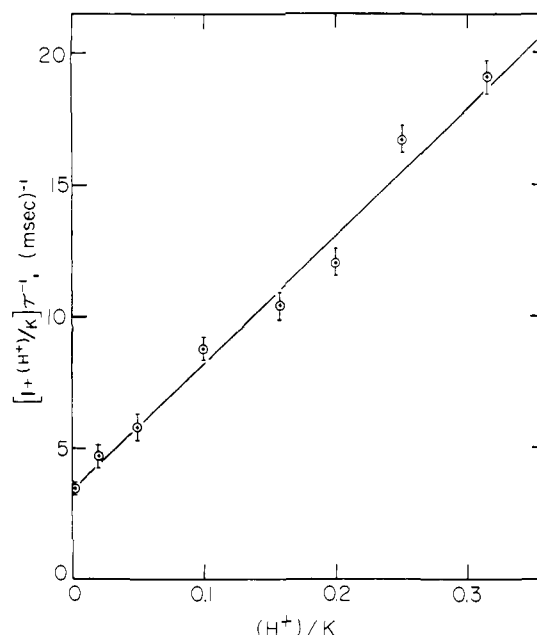
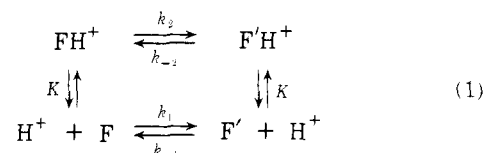


Figure 1. Plot of $[1 + (H^+)/K](1/\tau)^{-1}$ vs. $(H^+)/K$, for 0.1 M NaCl, 25 °C. Individual points are averages over a range of formycin concentration of 10 μ M to 1 mM. The line was determined by the method of least squares. Error brackets correspond to the range of observed values.

lecular process is responsible for the relaxation. However, the relaxation time τ shows a significant pH dependence that is most easily described by eq 1 where F and F' are formycin



tautomers. Assuming the vertical ionization steps are rapidly equilibrated (and have roughly similar pK values), the relaxation time for this mechanism is simply given by

$$[1 + (H^+)/K](1/\tau) = (k_1 + k_{-1}) + [(H^+)/K](k_2 + k_{-2}) \quad (2)$$

According to eq 2, a plot of $[1 + (H^+)/K](1/\tau)^{-1}$ vs. $(H^+)/K$ should yield a straight line with slope of $(k_2 + k_{-2})$ and an intercept of $(k_1 + k_{-1})$.

Figure 1 gives a plot of the data, according to eq 2. It is clear that a strictly linear relationship is obtained between $[1 + (H^+)/K](1/\tau)$ and $(H^+)/K$, where the spectrophotometrically determined (by us) value of $K = 10^{-4.5}$ was used. (This pK value (for N(6)) agrees well with other independent determinations.^{8,9}) From this plot we obtain (at 25 °C) $k_1 + k_{-1} = 3.4 \times 10^3 \text{ s}^{-1}$ and $k_2 + k_{-2} = 4.9 \times 10^4 \text{ s}^{-1}$. (Errors in values of $k_1 + k_{-1}$ and $k_2 + k_{-2}$ are estimated as $\pm 15\%$.) Thus, with formycin in the protonated form, tautomerization is much faster (also, see below). As far as we know, this is the first determination of tautomerization rate constants at 25 °C for these kind of compounds.

We assumed that the microscopic pK's for the two vertical ionization steps are identical. The data fit well with the simple assumption. Also, the data do not give a good fit if the single pK is varied beyond the range of $\text{pK} = 4.5 \pm 0.2$. If the two microscopic pK's are close in value, then there should be no uptake or release of protons accompanying the horizontal tautomerization steps. This expectation was confirmed by finding that the relaxation is not observed when one attempts to follow it by transient changes in a pH indicator. Since the two vertical ionization steps have about the same equilibrium