or no sensitization observed should be reconsidered. Triplet counting experiments and thus intersystem-crossing efficiencies could also show concentration effects.

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(9) National Aeronautics and Space Administration Trainee, 1966–1969.

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A Reversible Complex of Nitrous Oxide with Cobalt(II) Type-A Synthetic Zeolite

Sir:

Spectroscopically and chemically well-defined complexes have been observed in the $\mathrm{Ni^{II}}$A zeolites.[1] The $\mathrm{Ni^{II}}$ ions in a trigonal, almost planar coordination in the zeolitic network combine with various molecules such as olefins, acetylene, cyclopropane, and molecules having a permanent dipole. The $\mathrm{Co^{II}}$ ions have now been found to have similar properties, the spectral changes due to the complex formation being particularly striking.

One of the most interesting examples is the adsorption of nitrous oxide on a dehydrated $\mathrm{Co^{II}}$A zeolite which results in a spectral change shown in Figure 1.

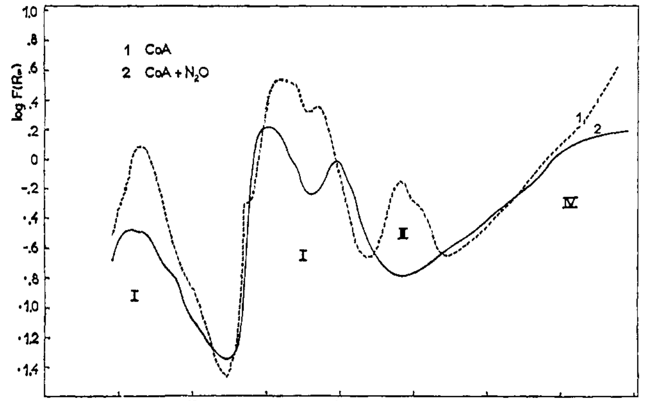

Figure 1. Spectrum of dehydrated, partially exchanged, $\mathrm{Co^{II}}$A zeolite without (curve 1) and with (curve 2) adsorbed nitrous oxide. The $\mathrm{Co^{II}}$A zeolite contained approximately one $\mathrm{Co^{II}}$ ion in one large cavity. N_2O was added at a pressure of about 400 Torr. $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$ is proportional to the absorption coefficient (K. Klier, *Catalysis Rev.*, **1**, 207 (1967)) and the wave number on the abscissa axis is given in $\mathrm{cm^{-1}}\ 10^{-3}$.

In analogy to the $\mathrm{Ni^{II}}$A zeolite, the spectrum 1 is interpreted as that of the $\mathrm{Co^{II}}$ ions in an almost planar trigonal coordination to the zeolitic oxygens, the bands I and II being caused by the spin-allowed d_{yz}, $d_{zx} \rightarrow d_{xy}$, $d_{x^2-y^2}$ transitions and the band III, by a $d_{z^2} \rightarrow d_{xy}$, $d_{x^2-y^2}$ transition.[2] The presence of an adsorbed molecule on the *z* axis perpendicular to the plane of oxygen ligands will primarily affect the energy of electrons in the d_{z^2} orbital with the result of shifting the band III to lower energies (Figure 1, curve 2). Since there are no signs of the residual $\mathrm{Co^{II}}$A spectrum 1 in the spectrum 2 of the N_2O–$\mathrm{Co^{II}}$A complex, it is concluded that all cobaltous ions have reacted with one nitrous oxide molecule each. Nitrous oxide can be desorbed by pumping at 50°, whereby the spectrum 1 is completely regenerated. Analysis of the desorbate shows that only N_2O molecules are present under these conditions. Therefore, the N_2O molecule as a whole, and not its fragments, is the reversible ligand to the $\mathrm{Co^{II}}$A zeolite.

At elevated temperature (150°), however, the nitrous oxide molecules decompose over the $\mathrm{Co^{II}}$A zeolite, and an equimolar mixture of $2N_2 + O_2$ is formed. The cobaltous ions are not oxidized during this process but evidently are catalyzing it. Since there is approximately one cobaltous ion in one cavity, the first product of N_2O decomposition must be a nitrogen molecule and an oxygen atom. We propose that this system offers interesting applications in selective oxidation catalysis, having the advantage of both separability of a heterogeneous catalyst from the reactants and uniform energetics of the reactant molecules known so far only in homogeneous catalysis.

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(1) K. Klier and M. Ralek, *J. Phys. Chem. Solids*, **29**, 951 (1968).

(2) These assignments are meaningful since it has been shown (R. Polak and K. Klier, *ibid.*, in press) that the low symmetry field behaves as a strong ligand field in all relevant cases.

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Alkyl Hex-2-enopyranosid-4-uloses. A New Class of Unsaturated Pyranosides

Sir:

This communication describes some stable, crystalline alkyl hex-2-enopyranosid-4-uloses (**2**), the first reported examples of incorporation of an α,β-unsaturated ketone functionality with high yield into an alkyl pyranoside unit.[1] These molecules are intriguing because the potential they possess for syntheses originating with α,β-unsaturated carbonyl compounds can now be explored as routes to the pharmacologically important branched-chain and amino sugars, the latter being important components of many major antibiotics.[3,4]

The allylic hydroxyl group of recently synthesized **1a**[5] was, as expected, readily oxidized by manganese dioxide[6-8] to ketone **2a** (50% yield; mp 70°; $[\alpha]^{23}\mathrm{D}$ $-7.7°$ (c 1.02, $\mathrm{CHCl_3}$); $\lambda_{\max}$ (log ϵ) 277 (4.17), 219 mμ (4.09); $\nu_{\max}$ 5.51, 5.99 μ). The ethyl analog **1b** obtained from **1c**[9,10] by selective benzoylation (*cf.*

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(1) Some interesting related systems have been reported,[2] particularly one[2a] which is formally the monoenol ester of an α diketone.

(2) (a) P. J. Benyon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc.*, 1131 (1960); (b) E. F. L. J. Anet, *Carbohyd. Res.*, **1**, 348 (1966); (c) E. F. L. J. Anet, *Aust. J. Chem.*, **15**, 503 (1962).

(3) F. Shafizadeh, *Advan. Carbohyd. Chem.*, **11**, 263 (1956).

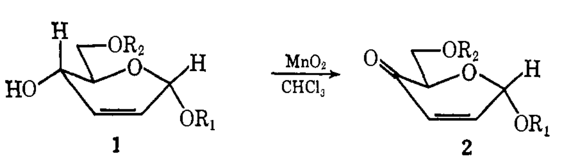
(4) R. U. Lemieux and M. L. Wolfrom, *ibid.*, **3**, 337 (1948).

(5) B. Fraser-Reid and B. Boctor, *Can. J. Chem.*, **47**, 393 (1969).

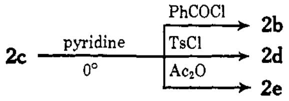
(6) E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968).

(7) H. B. Henbest, E. R. H. Jones, and T. C. Owen, *J. Chem. Soc.*, 4909 (1957).

(8) All new compounds gave satisfactory microanalyses and spectral data.



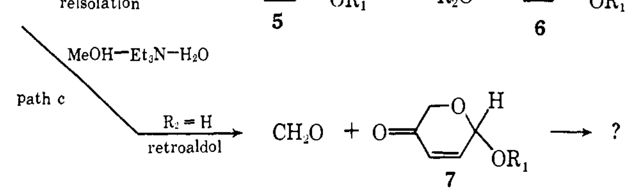
a, $R_1 = CH_3$; $R_2 = C_6H_5CO$
b, $R_1 = CH_2CH_3$; $R_2 = C_6H_5CO$
c, $R_1 = CH_2CH_3$; $R_2 = H$
d, $R_2 = Ts$
e, $R_2 = Ac$



ref 5) was likewise converted to **2b** in comparable yield. However, attempts to tosylate **1c** selectively at the primary alcohol were unsuccessful (*cf.* ref 11); it was therefore gratifying to find that despite its sensitivity to base (*vide infra*), ketone **2c** (mp 85–86°; $[\alpha]^{23}D$ −14.50° (c 2.06, $CHCl_3$); λ_{max} (log ϵ) 214 mμ (3.96); ν_{max} 2.78, 5.88, 6.10 μ), obtained in 80% yield by oxidation[6,7] of **1c**, could be tosylated, benzoylated, or acetylated in ice-cold pyridine solution to **2d**, **2b**, and **2e**, respectively.[8] In the nmr these substances display a diagnostic pattern for the annular protons as is demonstrated by the partial spectrum of **2a** reproduced in Figure 1a.

Syntheses involving α,β-unsaturated ketones frequently originate with base-induced enolization; therefore knowledge of the behavior of **2** toward base is of paramount importance. Two probable transformations of **2**—anomerization (**2** to **4**; path a) and conversion from the D-*glycero* to the L-*glycero* configuration (**2** to **6**; path b)—alter asymmetric centers (Scheme I), and

Scheme I



accordingly the optical rotation of **2a** in aqueous acetone containing triethylamine fell to a constant value after 3 hr.[12] The substance remaining after evaporation of the liquids from the equilibrated mixture was judged (ir, nmr, tlc, 2,4-dinitrophenylhydrazone) to contain **2a**[13] only and no **4** or **6**. The change in optical activity therefore implied the formation of one of the mutually exclusive alternatives **3** or **5**, and in order to determine which, the equilibration was monitored by nmr (Figure 1). The signals for H-2 and H-3 of **2a** (superimposed in Figure 1a) were shifted gradually to new locations, 0.14 ppm to lower field (Y′′ and X, respectively), although their *couplings* to H-2 were not measurably affected. These observations, substantiated by double-irradiation experiments (Figure 1b), suggested that the drastic alterations about C-1 and C-2 required by path a could not be occurring. Path b was therefore implicated and, consistently, the signal Y′, which is readily interpreted[14] as arising from the benzoyloxymethyl group of **5**,[17] grows at the expense of the multiplet for H-5, H-6, H-6 originally 0.76 ppm to higher field. Preferential operation of path b is not surprising since the carbanion resulting from removal of H-1 (path a) is flanked by two oxygen atoms, whereas that leading to **5** is adjacent to one oxygen atom only. The complete reversion of **5** to **2a** upon isolation portrays the serious nonbonded interactions which render **6** thermodynamically unfavorable.

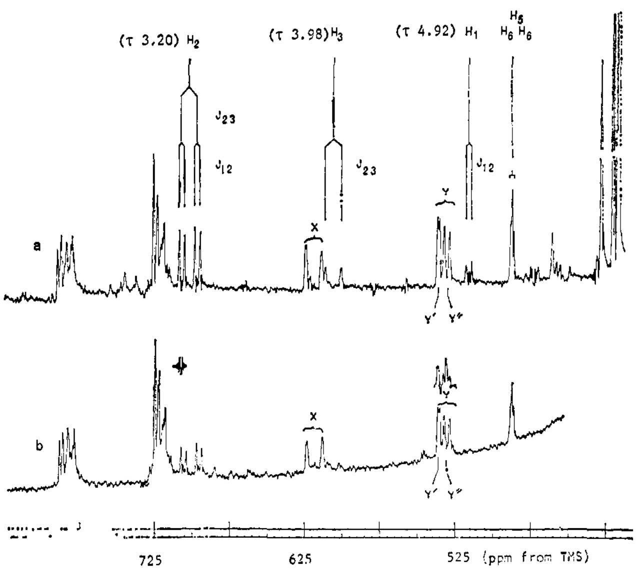


Figure 1. Nmr monitors of the reaction of **2a** with Me_2CO-Et_3N-D_2O at 100 MHz after 1 hr (a) and 3 hr (b) using Me_2CO as a lock signal with a sweep width of 500 Hz. The assignments and coupling constants (J_{12} = 3.5 Hz; J_{23} = 10.0 Hz) shown in spectrum a refer to **2a** run in $CDCl_3$ with chemical shift relevant to internal TMS.

Retroaldol elimination (Scheme I, path c) represents an alternative mode of reaction for **2** (R = H). Although formaldehyde liberation[18] from **2c** in aqueous methanol containing triethylamine was complete (80%

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(9) M. Bergmann, *Ann.*, **443**, 223 (1925).

(10) We are grateful to Dr. R. J. Ferrier for making details of his new synthesis of the diacetate of **1c** available to us prior to publication.

(11) S. Laland, W. G. Overend, and M. Stacey, *J. Chem. Soc.*, 738 (1950).

(12) For 30 mg of **2a** in 1 ml of Me_2CO-H_2O-Et_3N (6.0:2.0:0.25 v/v) mixture, observed rotation (min): −0.237° (2), −0.296° (15), −0.326° (30), −0.425° (60), −0.445° (90), −0.475° (120), −0.490° (150), −0.500° (180), −0.530° (240), −0.530° (480).

(13) Recovery based on the 2,4-dinitrophenylhydrazone was 72%. In the medium some debenzoylation is to be expected[5] and, on the basis of formaldehyde liberation (*vide infra*), this was determined to be 12%.

(14) The signal Y′ undoubtedly represents lines 2 and 3 of an AB system resulting from nonequivalence of the two H-6's of **5**. Using a value of J_{gem} = 12.6 Hz[15] and the observed spacing in Y′ (1.5 Hz) lines 1 and 4 are estimated[16] to be one-tenth as intense as lines 2 and 3. They would therefore be lost in the "noise."

(15) W. L. Meyer and R. B. Meyer, *J. Amer. Chem. Soc.*, **85**, 2170 (1963).

(16) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 2.

(17) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High-Resolution NMR Spectra Catalogue," Varian Associates, Palo Alto, Calif., 1962, spectra 34 and 43.

(18) T. Nash, *Biochem. J.*, **55**, 416 (1953).

theoretical yield) after 3 hr at room temperature, the product isolated gave no spectroscopic evidence compatible with **7**, but it contained a number of degradation products. In order to gain insight into the stability of **7**, the following synthesis was conducted. The product from the reaction of 3,4-di-*O*-acetyl-D-xylal[19] with $EtOH-BF_3-PhH$[10] was deacetylated, and the resulting anomers of ethyl D-*glycero*-pent-2-enopyranoside were separated[20] (plc). One of these[21a,c] was strangely inert to MnO_2 oxidation, a phenomenon currently under investigation; however, the other[21b,c] afforded an oily ketone[22] with ir, uv, and nmr characteristics consistent with those of **7** (or its anomer!). When the latter ketone was treated as above with water–methanol–triethylamine, the absorption at 214 mμ disappeared immediately, *but formaldehyde was not liberated.* The residue obtained upon isolation indicated drastic decomposition; however, comparison (tlc) with the material derived from **2c** showed several common components. Furthermore, its principal infrared absorptions were present also in the material from **2c**. *Significantly, the saturated ketone resulting from partial hydrogenation of* **2c** *does not produce formaldehyde when treated with triethylamine.* The dienolate ion of **7** initially formed in the retroaldol reaction of **2c** evidently provides the impetus for formaldehyde liberation.

Acknowledgment. We are grateful to the National Research Council of Canada for financial support and to Mr. Brian Sayer of McMaster University for the 100-MHz nmr determinations.

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(19) F. Weygand, "Methods of Carbohydrate Chemistry," Vol. 1, Academic Press, New York, N. Y., 1962.

(20) Each isomer was characterized as its 3,5-dinitrobenzoate.[8]

(21) (a) $[\alpha]^{23}\text{D}$ +44.3° (*c*, 5.8, chloroform); (b) $[\alpha]^{23}\text{D}$ +22.2° (*c*, 2.33; chloroform); (c) rigid assignment of these as α or β anomers awaits current X-ray crystallographic examination.

(22) Characterized as its semicarbazone.

(23) Undergraduate research participant.

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The Chromium(II) Reduction of *cis*-Dichlorotetraammineruthenium(III). A Reversible Electron Transfer Prior to the Rate-Limiting Step

Sir:

The details of inner-sphere electron-transfer reactions have usually been represented as a combination of three steps:[1-3] an association step in which the bridge between the two metal ions is formed, the nuclear rearrangement that leads to the change in oxidation state, and the decomposition of the resultant binuclear product. Direct information about these binuclear intermediates has been obtained in only a few systems. Newton and Baker have reviewed the evidence concerning those intermediates composed partly or wholly of actinide ions.[4] In most of these and other systems studied to date,[5,6] the decomposition of the product binuclear intermediate is an important kinetic step. Occasionally, H^+ dependencies have given some information concerning the reactivity of the intermediate.[4,7] However, systems in which formation of the product binuclear intermediate is reversible are unusual.[8] It is the observation of such a reversible system in which chloride ion serves as the bridge that prompts this communication.

$[Ru(NH_3)_4Cl_2]Cl\cdot{}^2/_3H_2O$ was prepared by the procedure of Gleu.[9] The compound was pure as evidenced by analysis for ruthenium (by persulfate ion oxidation to a mixture of RuO_4^{2-} and RuO_4^-, and spectrophotometric analysis at 4150 Å, an isosbestic point, ϵ 1075)[10] (*Anal.* Calcd: Ru, 35.2. Found: Ru, 35.2) and by spectrophotometric analysis (λ (ϵ): 3530 (1580), 3100 (1350), 2620 Å (500); lit.[11] 3520 (1640), 3100 (1380), 2620 Å (510). All kinetic experiments were run in 0.10 *N* *p*-toluenesulfonic acid in order to avoid ClO_4^- reduction by Ru(II).[12] Transmittance *vs.* time curves were obtained on a Durrum-Gibson stopped-flow spectrometer.

To establish the stoichiometry of the reaction, excess *cis*-$Ru(NH_3)_4Cl_2^+$ was allowed to react with Cr(II), and the spectrum of the resultant solution was obtained. The maximum at 6030 Å (ϵ 15 ± 2 M^{-1} cm^{-1}) is in good agreement with literature values for $CrCl^{2+}$ [13,14] and indicates this product results from the electron-transfer process. Blank experiments in which some *cis*-$Ru(NH_3)_4Cl_2^+$ was reduced by Cr(II) and then mixed with *cis*- and *trans*-$CrCl_2^+$, prepared by the method of King, *et al.*,[14] established the absence of Ru(II) catalysis of $CrCl_2^+$ aquation. The absence of a product derived from a dibridged transition state is consistent with the reduction by Cr(II) of another *cis*-dichloro system.[15]

The pseudo-first-order rate constants for the reduction of *cis*-$Ru(NH_3)_4Cl_2^+$ by Cr(II), k_{obsd}, are listed in Table I. It is apparent that the data do not fit the normal second-order rate law found for most electron-transfer reactions. Note, for instance, that run 6 has 20 times the $[Cr^{2+}]$ of run 8, whereas the first-order rate constant changes by less than a factor of 4. However, a plot of k_{obsd}^{-1} *vs.* $[Cr^{2+}]^{-1}$ gives a straight line with slope of 1.4×10^{-5} *M* sec and an intercept of 6.5×10^{-3} sec. The fit of the data to this plot is illustrated

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(2) H. Taube, "The Robert A. Welch Foundation Conferences on Chemical Research, VI," Houston, Texas, Nov 1962.

(3) R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc.*, **88**, 1872 (1966).

(4) T. W. Newton and F. B. Baker, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 268.

(5) See, for instance, (a) J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965); (b) R. K. Murmann and J. C. Sullivan, *ibid.*, **6**, 892 (1967), and references therein; (c) see also, H. Taube, *J. Chem. Educ.*, **45**, 452 (1968); (d) J. Stritar and H. Taube, private communication from Professor J. Stritar.

(6) R. N. F. Thorneley and A. G. Sykes, *Chem. Commun.*, 331 (1969); (b) D. Seewald and N. Sutin, Paper M005, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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(10) (a) S. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961); (b) E. V. Luoma and C. H. Brubaker, Jr., *Inorg. Chem.*, **5**, 1637 (1966).

(11) W. Hartman and C. Buschbeck, *Z. Physik. Chem.* (Frankfurt), **11**, 120 (1957).

(12) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962); *Inorg. Chem.*, **4**, 437 (1965).

(13) J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965), report $\lambda_{\max}$ 6070 Å (ϵ 16.4 M^{-1} cm^{-1}); *cis*-$CrCl_2^+$ has $\lambda_{\max}$ 6400 Å (ϵ 19.6).[14]

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