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

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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 $Ni^{II}A$ zeolites.[1] The 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 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 $Co^{II}A$ zeolite which results in a spectral change shown in Figure 1.

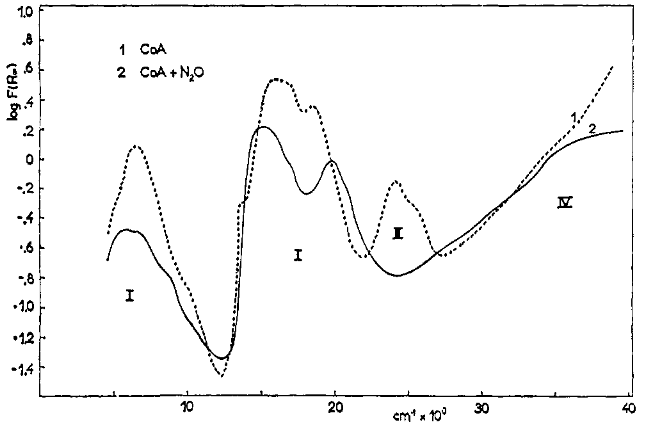

Figure 1. Spectrum of dehydrated, partially exchanged, $Co^{II}A$ zeolite without (curve 1) and with (curve 2) adsorbed nitrous oxide. The $Co^{II}A$ zeolite contained approximately one Co^{II} ion in one large cavity. N_2O was added at a pressure of about 400 Torr. $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$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

In analogy to the $Ni^{II}A$ zeolite, the spectrum 1 is interpreted as that of the 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 $Co^{II}A$ spectrum 1 in the spectrum 2 of the N_2O–$Co^{II}A$ 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 $Co^{II}A$ zeolite.

At elevated temperature (150°), however, the nitrous oxide molecules decompose over the $Co^{II}A$ 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.

(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°; $[\alpha]^{23}D$ $-7.7°$ (c 1.02, $CHCl_3$); λ_{max} (log ϵ) 277 (4.17), 219 mμ (4.09); ν_{max} 5.51, 5.99 μ). The ethyl analog **1b** obtained from **1c**[9,10] by selective benzoylation (*cf.*

(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.