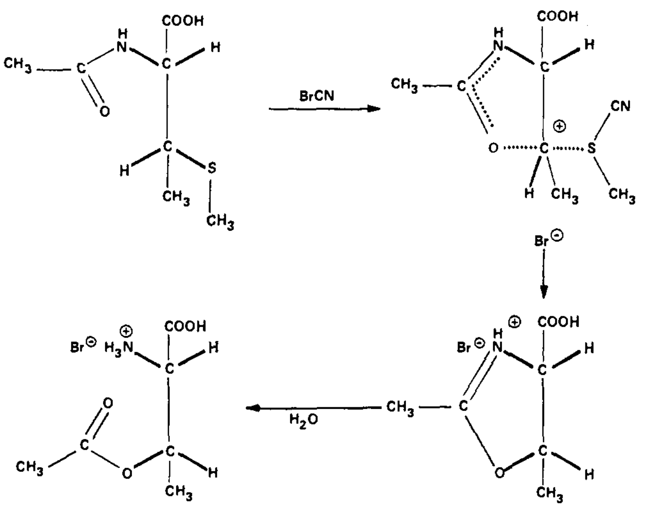

Figure 1. The reaction of *N*-acetyl-β-methyl-*S*-methylcysteine with cyanogen bromide.

acid analysis indicated an initial 5% per day rate of formation of β-methyllanthionine. The only side reaction of significance, the formation of serine, proceeded at half that rate. The products from DL-*threo*-β-methylcysteine are not separated in the chromatographic system employed (peak II, Figure 2); those from DL-*allo*-β-methylcysteine are eluted at different effluent volumes (peaks I and I′, Figure 2).[9]

The isomer of β-methyllanthionine occurring in nisin[2] coelutes with the threo derivatives and must therefore have the L-*configuration at the β-carbon atom* since the α-carbon atom of the amino butyric acid moiety had previously been assigned the D configuration.[2]

Inasmuch as the assignment of configuration is based on properties of the amino acids obtained by acid hydrolysis, knowledge of the extent of racemization occurring under these conditions is necessary. Lanthionine is completely racemized under the conditions of acid hydrolysis.[2] Isolation of the isomers represented by peak I′ and treatment with 6 *N* HCl for 24 hr at 110° results in the transformation of 30% of the material to the isomers of peak I and 10% to the isomers of peak II. When the isomers of peak II are exposed to the same conditions, they are transformed to the extent of 10% to the isomers of peaks I and I′.

Evidently the α-carbon atom of the alanine moiety is subject to more extensive configurational change than that of the amino butyric acid portion. This is consistent with the occurrence of 0.5 residues of *allo*-β-methyllanthionine in hydrolysates of nisin which contains a total of four residues of the amino acid. Thus, only 63% of the amino acid in a hydrolysate retains the original configurations, while 27% is inverted at the alanine moiety alone, 3% at both the α-carbon atoms of the alanine and amino butyric acid portions, and 7% at the α-carbon atom of the amino butyric acid moiety only. In spite of this, β-methyllanthionine having the correct configuration at the α-carbon atoms[3] and showing the elution behavior of the threo compound[10] was isolated by the selective process of crystallization from a hydrolysate of subtilin.[11]

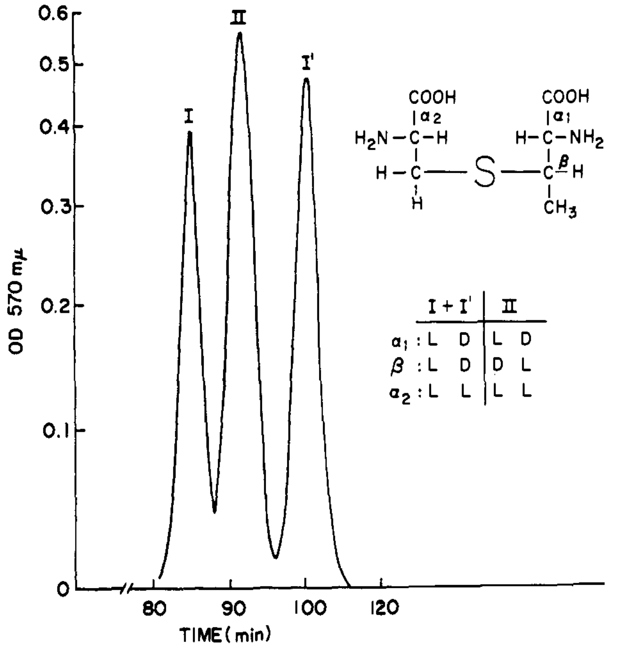

Figure 2. The separation of the isomers of β-methyllanthionine by ion exchange chromatography (column: 0.9 × 60 cm, 53°, 0.2 *N* sodium citrate buffer, pH 3.25). Isomers not shown in inset are enantiomers with the D-alanine moiety.

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[8] This procedure gave 95% pure L-lanthionine in a trial synthesis wherein the undesired product of epimerization (*meso*-lanthionine) is easily detected by ion exchange chromatography.

[9] In a synthesis involving addition of DL-cysteine to benzoyldehydrobutyrineazlactone, the quantities of the isomers of peaks I, II, and I′ are in the proportion 1 : 2 : 1.

(10) A. Schöberl, E. Gross, J. L. Morell, and B. Witkop, *Biochim. Biophys. Acta*, **121**, 406 (1966).

(11) G. Alderton, *J. Amer. Chem. Soc.*, **75**, 2391 (1953).

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Fe[OAl(O-*n*-Bu)$_2$]$_2$. A New Molecular Oxygen Activator

Sir:

We want to report the behavior of an oxo alkoxide of aluminum and iron(II) as a reversible molecular oxygen activator.

This amorphous compound, highly soluble in hydrocarbons, is obtained by a straight condensation reaction (at 500°K in decalin under argon atmosphere), according to eq 1. Its composition was established by

$$2Al(OR)_3 + Fe^{II}(CH_3COO)_2 \longrightarrow (OR)_2AlOFeOAl(OR)_2 + 2CH_3COOR \quad (1)$$

elementary analysis;[1] the Al/Fe ratio is found to be near 1.98 by complexometric titration (EDTA in acetate buffer after oxidation of Fe(II) into Fe(III)). The OR/Al ratio as determined by glc after hydrolysis of the complex equals 1.96. All these values are consistent with the expected ones for eq 1, *i.e.*, Al/Fe = OR/Al = 2. R may be a *n*-butyl, isopropyl, or isobutyl group. Other oxo alkoxides may also be prepared in the same

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(1) M. Osgan and Ph. Teyssié, *J. Polym. Sci., Part B*, **5**, 789 (1967); T. Ouhadi, A. J. Hubert, and Ph. Teyssié, to be submitted for publication.

way with Zn, Co(II), Mn(II), or Mo(II), instead of Fe(II); however, these latter compounds may have physical, chemical, and catalytic properties significantly different from the aluminum–iron complex.

Oxygen binding by this iron oxo alkoxide in heptane solution at 298°K occurs rapidly until a O_2/Fe ratio of about 0.25; then a slower absorption is observed until a final O_2/Fe (0.5) ratio is reached.

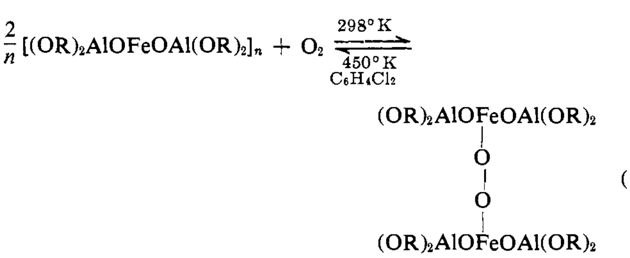
The kinetics of molecular oxygen absorption do not correspond to any simple reaction order process, most probably as the degree of association of the oxo alkoxide molecules in solution changes from $n = 8$ (initial complex) down to $n = 2$ (completely oxidized complex) in the course of the oxygen absorption process (cryoscopic measurements).

The oxidized compound behaves as a strong peroxidic oxidation agent toward KI in 10 N hydrochloric acid, immediate and quantitative oxidation of iodide to I_2 occurring under argon at 373°K (two molecules of I_2 per molecule of complex I).

Oxygen may also be swept off quantitatively by refluxing the complex in *o*-dichlorobenzene. Upon oxidation, the solution which is initially green (in heptane or other solvents) turns red; refluxing in $C_6H_4Cl_2$ yields back the initial green coloration and the process may be repeated several times.

By redox titration, Fe(II) is found to be the dominant species in the unoxidized complex, while, after O_2 absorption, Fe(III) is the only valence state as observed by a specific EDTA complexometric titration. This valency change of Fe is supported by uv–visible spectra which show a band at 950 nm in the unoxidized complex; this band, characteristic of the high-spin Fe(II) complexes and assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition,[2] disappears upon oxidation.

Supported by the former data, a reversible oxygen transport mechanism (eq 2) may be postulated.



$$\frac{2}{n}[(OR)_2AlOFeOAl(OR)_2]_n + O_2 \underset{C_6H_4Cl_2}{\overset{298°K}{\underset{450°K}{\rightleftharpoons}}} \begin{matrix} (OR)_2AlOFeOAl(OR)_2 \\ | \\ O \\ | \\ O \\ | \\ (OR)_2AlOFeOAl(OR)_2 \end{matrix} \quad (2)$$

I

The reversibility of a mechanism such as eq 2 (with respect to Fe) has been ascertained over four complete redox cycles from epr data. No signal is detected for the unoxidized material at 298°K; hence, this species probably contains Fe(II) which is not detected by epr at this temperature. Upon oxidation, a broad resonance line (peak-to-peak line width = 1500 Oe) centered near $g = 2.3$ appears gradually. Internal calibration with respect to a known standard (Varian Strong Pitch) was used to evaluate the relative spectral intensities and to show that the epr signal was of the order of magnitude expected for the oxidized compound in solution at the used concentration level, hence ruling out impurity effects; this signal is assigned to Fe(III) species.

The epr signal of the oxidized solid compound has an intensity which is nearly independent of temperature in the range 77–320°K. The behavior of this signal compares itself quantitatively to that reported for Fe(III) in zeolites;[3] accordingly, we propose that the solid compound shows ferromagnetic behavior.

From a catalytic standpoint, this reversible oxidation of the ferrous ions, associated with oxygen transport, seems quite interesting and rather unusual; to our knowledge, very few similar examples have been reported: one in the case of heterogeneous catalysts[4] and another one for a soluble complex.[5]

Acknowledgment. The authors are indebted to the Institut Français du Pétrole for financial support.

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[3] L. S. Singer and D. N. Stamires, *J. Chem. Phys.*, **42**, 3299 (1965).

[4] R. L. Garten, W. N. Delgass, and M. Boudart, *J. Catal.*, **18**, 90 (1970).

[5] L. Vaska, Abstracts of the American Chemical Society Summer Symposium on Coordination and Activation of Small Molecules by Transition Metals, Buffalo, N. Y., June 1972.

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A General Method for the Determination of Steric Effects during Collisional Energy Transfer. Partial Photoresolution of Penta-2,3-diene

Sir:

Since an electronically excited sensitizer (P*) and a quencher (A) must be very close during collisional energy transfer, bulky groups close to the chromophores of P and A should be important in determining the efficiency of transfer. Demonstration of such effects has proved difficult[1] and only in a few cases have they been reported.[2,3] The main problem has been to separate a group's electronic pertubation on a chromophore (auxochromic effect) from its steric influence on the ease of approach of another molecule. We have devised a general method for the study of steric influences on collisional energy transfer which excludes auxochromic effects.[4] We report here its first application: the partial photoresolution of penta-2,3-diene (**1**).

Since the energy levels of any pair of enantiomeric allenes are the same, the rate constants for energy transfer from a nonchiral P to (*R*)- and (*S*)-**1** must be identical (*i.e.*, $k_r = k_s$). When P is optically active, k_r and k_s need not be equal. The collision complexes, $[P\cdots(S)\text{-}\mathbf{1}]^*$ and $[P\cdots(R)\text{-}\mathbf{1}]^*$ are diastereomeric and, in principal, chemically distinguishable. We have mea-

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[1] See, for example, P. J. Wagner, J. M. Mc Grath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972).

[2] (a) G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965); (b) W. G. Herkstoeter, L. B. Jones, and G. S. Hammond, *ibid.*, **88**, 4777 (1966).

[3] K. Janda and T. S. Wattack, *ibid.*, **94**, 305 (1972).

[4] The work of Hammond and Cole, ref 2a, originally led us to consider this problem. Their system, except for the existence of a meso form of their quencher, would have allowed exactly the same treatment as applied here. We thank Professor Hammond for helpful discussions. For a pertinent, theoretical discussion of asymmetric inductions, see L. Salem, *J. Amer. Chem. Soc.*, **95**, 94 (1973).