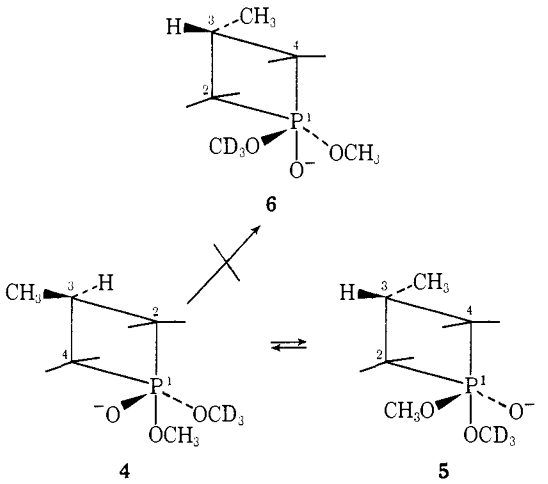
observed (within the error limits of nmr integration, about ±5%).[8] Indeed no interconversion of the isomers was observed after 24 hr at 60°. Thus exchange occurs in each isomer with retention of configuration[9] and without isomer crossover.

Attack of $CH_3O^-$ along an apical coordinate (*i.e.*, the P–$C_2$ bond[10]) of **1** (*trans*, R = $CD_3O$) gives intermediate[11] **4** which leads to **5** by pseudorotation (using $O^-$ as a pivot group).[12] Displacement of $CD_3O^-$ from an apical position in **5** (requirement of microscopic reversibility[11b]) yields the *trans* ester. Alternatively, pseudorotation of **4** to give **6** is unlikely for the electron-donating $O^-$ is in an energetically unfavorable position.[11b,13] Also, **6** would ultimately lead (by further pseudorotation) to isomer crossover, which was not observed.

Equatorial attack by methoxide on **1** (*trans*) can occur from the same or opposite side of the 3-methyl group to give the mirror image of **6** and **5**, respectively. Pseudorotation of the mirror image of **5** ($O^-$ pivot) gives the mirror image of **4** which produces **1** (*trans*) on equatorial departure of $CD_3O^-$; however, as the group leaves, the apical $CH_3O$ undergoes a 65–70° angle change[14] in going to **1** (*trans*). This angle change does not apply to the "apical-in-out" mechanism (**4** → **5** → **1** (*trans*)) which may therefore be regarded as the energetically favored process.[11b,13]



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[8] The per cent deuterium exchange and lack of isomer crossover was followed in the nmr. In $NaOCH_3$–$CH_3OH$ solution pure **1** (*trans*) showed peaks (TMS reference) at τ 6.21 (d, $CH_3O$), 8.60 (s, 6 H, $PCCH_3$), and 8.92 (s, 6 H, $PCCH_3$); the last two values occur from overlap of two doublets (in benzene all four lines are evident; see text). Thus, the per cent exchange in *trans*-**1** (R = $CD_3O$) was followed by integration of the area in the methoxy region (initially zero) relative to either and/or both of the upfield methyl peaks at τ 8.60 and 8.92. No detectable amount of **1** (*cis*) appeared in this or the control run (R = $CH_3O$) in either the methoxy or upfield methyl region (see below). The *cis* ester (in a mixture of isomers in $NaOCH_3$–$CH_3OH$) showed characteristic peaks at τ (center) 8.69 (d, 6 H, $PCCH_3$), 8.82 (d, 6 H, $PCCH_3$), and 6.30 (d, $CH_3O$). The $^{31}P$–$^1H$ coupling constants in $NaOCH_3$–$CH_3OH$ were nearly the same (within ±1 Hz) as in benzene. At 100- and 250-Hz sweep width the $CH_3O$ peaks from **1** (*cis*) and **1** (*trans*) in a mixture were separable to the base line; likewise the peak at τ 8.60 (s, *trans*) was flanked on each side by the lower field half of the doublet at τ 8.69 (*cis*) and the lower field half of the doublet at 8.82 (*cis*); separation was very close to the base line. The per cent exchange in the *cis* isomer was followed by integration of the $CH_3O$ doublet (τ 6.30) relative to the methyl region (either and/or both τ 8.69 and 8.82); the analogous ratio for the *trans* ester in the mixture was also determined in a similar manner. In the exchange study, the area ratio of τ 8.69 (or 8.82) to 8.60 remained constant; this also held for the control mixture of **1** (R = $CH_3O$). Moreover, the area ratio of the *cis*:*trans* esters in the methoxy region of the control remained constant and provided an additional check on the lack of isomer interconversion.

[9] Similarly, treatment of **2** (*trans*) with phenyllithium to give the 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide,[5,7] mp 127°, must also go with predominant (minimum of 90%)[7] retention. This is now *unambiguously* established since the X-ray of the above oxide has been carried out [C. N. Caughlan and M. Haque, *Chem. Commun.*, 1228 (1968)]; Professor Caughlan has informed us that the *trans* structure (1-phenyl and 3-methyl) is correct and that the word "*cis*" in his manuscript was in error and should be "*trans*."

[10] Attack along the P–$C_4$ bond produces the mirror image of **4**.

[11] The ring spans the equatorial–apical positions in a trigonal bipyramid. An equatorial–equatorial relation (120°) would be highly strained. For pertinent references see: (a) P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968); (b) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (c) K. E. DeBruin, K. Nauman, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7031 (1969).

[12] Although the *trans* isomer is used as an illustration, the *cis* compound can be used with parallel conclusions.

[13] P. C. Van der Voorn and R. S. Drago, *ibid.*, **88**, 3255 (1966); D. S. Frank and D. A. Usher, *ibid.*, **89**, 6360 (1967); D. B. Boyd, *ibid.*, **91**, 1200 (1969), and references cited therein.

[14] This is an approximation based on X-ray data from 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide,[9] the acid **3** [D. D. Swank and C. N. Caughlan, *Chem. Commun.*, 1051 (1968)], and a related phosphonium salt [C. Moret and L. M. Trefonas, *J. Am. Chem. Soc.*, **91**, 2255 (1969)].

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## Characterization of $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$, the Product of an Arrested Friedel–Crafts Sulfination of Butadieneiron Tricarbonyl[1]

*Sir:*

Recent studies on the protonation of diene complexes of iron tricarbonyl using $HSO_3F$–$SO_2$ at low temperature[2] have prompted us to investigate systems in which Lewis acids other than the proton are present.

$BF_3$ gas was bubbled into a yellow solution of butadieneiron tricarbonyl (2.00 g) in 3.5 ml of liquid $SO_2$ under nitrogen at −30°. A brown coloration and a precipitate were produced; excess $BF_3$ and solvent were then allowed to escape while the mixture was slowly warmed to room temperature. Pumping at 0.5 Torr left an essentially quantitative yield (3.39 g) of the title compound (I) as a yellow solid,[3] mp 136–140° dec.

Crystals of I were grown under nitrogen from a solution in 1:2 nitromethane–dichloromethane over which was placed a layer of *n*-hexane. The slow diffusion of the latter into the solvent mix, accompanied by gradual cooling (+25 to −10° over 24 hr), provided the necessary controlled lowering of solubility. Yellow needle-like parallelepipeds, crystallizing in the noncentrosymmetric monoclinic space group $P2_1$ ($C_2^2$; no. 4) were obtained. Unit cell data are: $a = 6.58$ Å, $b = 11.78$ Å, $c = 7.40$ Å, $\beta = 92.41°$, $\rho_{\text{obsd}} = 1.79 \pm 0.05$ g cm$^{-3}$,[4] $\rho_{\text{calcd}} = 1.886$ g cm$^{-3}$ for $M = 325.84$ and $Z = 2$.

Complete X-ray diffraction data to $\sin\theta = 0.40$ (Mo Kα radiation, $\bar{\lambda}$ 0.7107 Å) were collected with a 0.01° incrementing Supper-Pace Buerger automated diffractometer, using a stationary background, ω-scan, stationary-background counting sequence. The structure was solved by a combination of Patterson, Fourier,

[1] This work was supported by NSF Grant GP-8077, ARPA Contract SD-88 (M. R. C.), and USPHS Grant GM-14336 (H. D. K.).

[2] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Am. Chem. Soc.*, **91**, 6968 (1969), and references cited therein.

[3] *Anal.* Calcd for I: C, 25.80; H, 1.86. Found (Miss Heather King, Microanalyst, Department of Chemistry, UCLA): C, 26.02; H, 2.05%.

[4] The density was measured by flotation in a bromoform–hexane mixture.

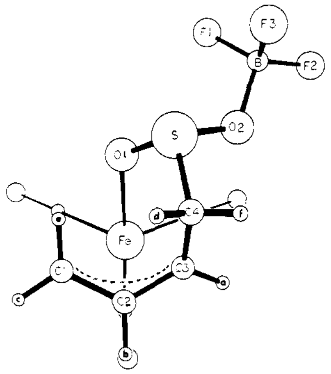

Figure 1. Projection of the $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$ molecule onto the plane defined by the three oxygen atoms of the $Fe(CO)_3$ group; the B–F distances are (±0.021 Å): B–F(1) = 1.389; B–F(2) = 1.335, and B–F(3) = 1.335. Other dimensions are given in the text.

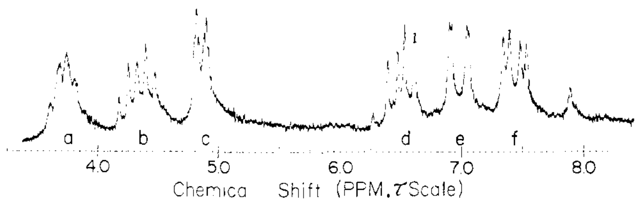

Figure 2. Proton magnetic resonance spectrum of $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$, 100 Mc, $SO_2$ solution at 25° (sealed tube). Chemical shifts (ppm, $\tau$ scale) are as follows: (a) 3.75, (b) 4.38, (c) 4.85, (d) 6.50, (e) 6.98, and (f) 7.44. For explanation of assignments and for values of coupling constants, see text.

and least-squares refinement techniques. Using anisotropic thermal parameters for all nonhydrogen atoms and including hydrogen atoms in calculated positions, the final discrepancy index was $R_F = 6.60\%$ for the 813 independent nonzero reflections.

The molecule is shown in Figure 1. The central iron atom is linked to three carbonyl ligands, a $\pi$-allyl system (individual iron–carbon distances are Fe–C(1) = 2.19 ± 0.02, Fe–C(2) = 2.09 ± 0.02, Fe–C(3) = 2.20 ± 0.02, and Fe···C(4) = 3.05 ± 0.02 Å), and to an oxygen atom of the inserted sulfur dioxide molecule (Fe–O(1) = 2.00 ± 0.01 Å).

Bond distances within the modified butadiene system are (Å): C(1)–C(2) = 1.44 ± 0.02, C(2)–C(3) = 1.42 ± 0.02 (in the range observed for $\pi$-allyl groups[5]), and C(3)–C(4) = 1.48 ± 0.02 (which is close to the average value for a C($sp^2$)–C($sp^3$) distance, 1.510 ± 0.005[6]).

The proton magnetic resonance spectrum of I is shown in Figure 2. The multiplets are labeled according to the letter assignments of the protons shown in Figure 1. The assignment of resonances assisted by comparison with the spectra of the similarly prepared $SO_2BF_3$ adducts of the iron tricarbonyl complexes of *trans*-1-methylbutadiene[7] (and a sample 90% enriched with the dideuterio derivative,[2] $CH_3CH{=}CHCH{=}CD_2$), 2,3-dimethylbutadiene, and *trans,trans*-1,4-dimethylbutadiene. The resonances of the $\pi$-allyl moiety are at lower field, except for the "inside" terminal proton, e, which is shifted by a characteristic[8] 2.13 ppm to higher field relative to the "outside" proton, c.

The coupling constants also reflect the structural features of the hydrocarbon group. Typical values[8] are observed around the $\pi$-allyl group (Hz): $J_{be}$ (*trans*) = 14.1; $J_{ab}$ (*cis*) $\sim$ 7, $J_{bc}$ (*cis*) = 8.9, and $J_{ce}$ (*gem*) = 1.9. As expected, a large coupling constant, $J_{df}$ = 13.8 Hz, is observed between *gem* protons of the saturated S-bonded atom, C(4). The vicinal couplings, $J_{ad}$ = 8.4 Hz and $J_{af}$ = 5.1 Hz, are in agreement with the larger and smaller dihedral angles between these protons ($\phi_{ad} \sim 155°$ and $\phi_{af} \sim 32°$, respectively[9]).

The remaining portion of molecule I may be recognized as a sulfinate group coordinated both to the metal atom and to a $BF_3$ molecule. The C(4)–S distance of 1.82 ± 0.02 Å is consistent with the recognized[6] value of 1.817 ± 0.005 Å for a carbon–sulfur single bond. Angles around the sulfur (O(1)–S–C(4) = 100 ± 1°, O(2)–S–C(4) = 98 ± 1°, and O(1)–S–O(2) = 109 ± 1°) suggest $sp^3$ hybridization. The sulfur–oxygen distances (S–O(1) = 1.50 ± 0.01 Å, S–O(2) = 1.54 ± 0.01 Å) are significantly lengthened from those of 1.4321 Å in gaseous $SO_2$.[10] One oxygen atom of the sulfinate group is coordinated to the iron atom and the other to a $BF_3$ molecule (B–O(2) = 1.50 ± 0.02 Å). The angles around the oxygen atoms are Fe–O(1)–S = 120 ± 1° and S–O(2)–B = 118 ± 1°.

Three bands are observed for I in the carbonyl stretching region of the infrared ($CH_2Cl_2$ solution, Beckman IR4, LiF prism) at 2116, 2074, and 2039 $cm^{-1}$. These bands are shifted to higher energy relative to the carbonyl stretching absorptions in butadieneiron tricarbonyl (2050, 1978 $cm^{-1}$), reflecting the considerable electron-withdrawing properties of the coordinated $\pi$-allylsulfinate group.

The title compound is best understood as the product of an electrophilic attack on terminal carbon in butadieneiron tricarbonyl by the $SO_2 \cdot BF_3$ adduct[11] formed below room temperature. We may therefore regard the reaction as an arrested Friedel–Crafts sulfination.[12] [An example of a Friedel–Crafts sulfination with the system $SO_2$–$HSO_3F$–$SbF_5$ has recently been reported.[13]] It occurred to us that a similar reaction should be possible with the adduct $SO_2 \cdot SbF_5$,[14] and we have isolated butadiene–$Fe(CO)_3 \cdot SO_2 \cdot SbF_5$ (II) whose proton nmr and infrared carbonyl spectra are analogous,[15] although not superposable, with those obtained for the $SO_2 \cdot BF_3$ complex. We therefore assume a structure similar to that found for I above, in which the $SbF_5$ group is present in place of the $BF_3$ group. Fur-

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(7) It is clear that the $SO_2 \cdot BF_3$ group is bonded to the terminal $CH_2$ or $CD_2$ group rather than to the terminal $CH(CH_3)$ group. A similar specificity is observed in protonation studies (see ref 2).

(8) See Table XIII in M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 72 (1965); K. Vrieze, *et al.*, *Rec. Trav. Chim. Pays-Bas*, **85**, 1077 (1966).

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(12) See, for instance, G. A. Olah," Friedel–Crafts and Related Reactions," Vol. 1, Interscience Publishers, New York, N. Y., Chapter 2.

(13) M. Brookhart, F. A. L. Anet, and S. Winstein, *J. Am. Chem Soc.*, **88**, 5657 (1966).

(14) (a) A. Commeyras and G. A. Olah, *ibid.*, **91**, 2929 (1969); (b) J. W. Moore, H. W. Baird, and H. B. Miller, *ibid.*, **90**, 1358 (1968).

(15) For compound II, $\tau$ (ppm): $H_a$ 3.68, $H_b$ 4.25, $H_c$ 4.70, $H_d$ 6.24, $H_e$ 6.93, $H_f$ 7.23, coupling constants Hz: $J_{ab} \sim 7$, $J_{ab} = 1.9$, $J_{ad} = 8.2$, $J_{af} = 4.9$, $J_{bc} = 8.5$, $J_{be} = 1.4$, $J_{ce} = 2.0$, $J_{df} = 14.5$; $\nu_{CO}$ 2120, 2077, 2044 $cm^{-1}$.

ther work on these and related derivatives, including attempts to isolate the metal–sulfinate species free of Lewis acid, are presently in progress.

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(16) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

(17) In receipt of a Graduate National Fellowship from Harvard University, 1968–1969.

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## Photosensitized Inactivation of Alanine Transfer RNA

*Sir:*

Several recent reports have indicated that photochemical dimerization of pyrimidines can be achieved by ketone-sensitized energy transfer without concomitant photohydration.[1–4] Application of this technique to DNA by Lamola and Yamane has provided the first example of photosensitized thymine–thymine dimer formation in a nucleic acid.[5] Because of the potential usefulness of sensitized pyrimidine photochemistry as a structure–action probe, we have examined this procedure with tRNA. We have found that the aminoacyl acceptor activities of $\mathrm{tRNA}^{\mathrm{Ala}}_{\mathrm{Iab}}$, $\mathrm{tRNA}^{\mathrm{Ala}}_{\mathrm{II}}$, and $\mathrm{tRNA}^{\mathrm{Tyr}}$ from yeast are inactivated rapidly by acetone-sensitized photochemistry. This communication describes our initial studies on acetone-sensitized photomodification of $\mathrm{tRNA}^{\mathrm{Ala}}_{\mathrm{Iab}}$. The results suggest that inactivation is caused by pyrimidine dimers formed by energy transfer from acetone to tRNA.

Commercial bakers yeast tRNA was fractionated as described previously, and $\mathrm{tRNA}^{\mathrm{Ala}}_{\mathrm{Iab}}$ of 94% purity was obtained.[6] Acetone-sensitized photolysis was carried out at 310 ± 10 nm with a Bausch and Lomb high-intensity, grating monochromator and a super-pressure mercury lamp. The monochromator was fitted with a quartz, plano-convex, collecting lens (1.5-in. i.d., 5-cm F.L. Model A-11-651-20, Oriel Optics Corp., Stamford, Conn.) and Corning 0-54 and 7-54 glass filters (Corning Glass Works, Corning, N. Y.), giving a window (97% transmission) between 304 and 410 nm. Under these conditions acetone was the only absorbing species in the reaction mixture. Irradiations were carried out in stoppered 1-cm light-path quartz cuvettes. The solutions were deoxygenated with $N_2$ and stirred mechanically during the irradiation. The acetone concentration in the reaction mixture was calculated from the absorbance at 300 nm and the molar extinction coefficient, $\epsilon_{300}$ 2.01 l./(mol cm). Actinometry performed with ferrioxalate[7] gave $I_0 = 0.13\ \mu$E/min.

In a typical experiment, a solution (3.2 ml) containing $\mathrm{tRNA}^{\mathrm{Ala}}_{\mathrm{Iab}}$ ($1.3 \times 10^{-3}$ *M*), $\mathrm{MgCl_2}$ ($10^{-2}$ *M*), and acetone (0.085 *M*) was irradiated as described above. Half the alanine acceptor activity[6] was lost after about 90 min. Loss of activity did not occur in the absence of acetone or with acetone in the dark. The rate of inactivation was dependent upon the acetone concentration, but for technical reasons the kinetic order is still uncertain. We wish to defer discussion of this important point until we are able to gather more data. It is clear, however, that the inactivation is sufficiently rapid at low acetone concentrations to be useful in structure–action studies.

These results show that the inactivation of tRNA is dependent upon acetone photochemistry. Two different processes might be involved: (1) energy transfer from excited acetone to tRNA followed by photochemistry of the excited tRNA to form pyrimidine dimers or possibly dihydropyrimidines[8] or (2) addition of excited acetone to tRNA to form oxetanes with uracil or cytosine.[2]

The role of photoaddition in the inactivation process was examined with acetone-2-$^{14}$C (specific activity 0.46 Ci/mol) under the conditions described above. After irradiation for 2.5 hr the acetone was removed from the reaction mixture by repeated evaporation *in vacuo* in the presence of added unlabeled acetone. Nonvolatile radioactive impurities were separated from the tRNA on benzoylated DEAE-cellulose[9] as described previously.[6] A large, radioactive, nonultraviolet absorbing peak was eluted with 85 ml of solution I.[6] A nonradioactive, ultraviolet absorbing peak was eluted between 79 and 120 ml of solution I. The exact nature of the material in these peaks is unknown, but they are not tRNA. After 120 ml of solution I had passed through the column, solution II[6] was started, and tRNA was eluted between 110 and 340 ml of this solution.

The pooled tRNA peak accounted for 91% of the material used in the reaction. It had only 15% of its initial alanine acceptor activity. Its specific radioactivity was 0.023 Ci/mol of tRNA, which corresponds to 0.05 mol of acetone adduct/mol of tRNA. Therefore, acetone addition is not a significant cause of inactivation under these conditions, and most, if not all, the inactivation is caused by energy transfer.

Although the evidence presented here is indirect, the most reasonable interpretation of the data in terms of current knowledge is that dimerization of adjacent pyrimidines causes inactivation of the tRNA. This conclusion is consistent with earlier observations which show that formation of a single dimer is sufficient, though not necessary, for the inactivation of $\mathrm{tRNA}^{\mathrm{Ala}}_{\mathrm{Iab}}$ by *direct irradiation* at 254 nm.[10]

These findings have important implications for structure–action studies on tRNA. Irradiation at 254 nm produces pyrimidine dimers and photohydrates.[10] This leads to very complex photochemistry because

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