

It is not possible to exactly evaluate the separate factors in eq 9, since pure monochromatic irradiation was not used and the value of  $k_{-t}$  has to be estimated. However, the expression in parentheses in the numerator can be estimated to equal 2.6, while the denominator equals approximately 0.8.<sup>18</sup> Consequently, the final slope in Figure 1 should equal roughly three-four times the normal  $k_q\tau$  value, as is actually observed.

Finally, it should be pointed out that the mixed ketone quenching plot in Figure 2 would be expected to begin curving upward at sufficiently high quencher concentrations that energy transfer from NB to NA began to be prevented.

These results specifically illustrate two predictable complications in the decay kinetics of systems containing more than one chromophore. If there is any energy transfer between chromophores, the observed decay rate of any one chromophore no longer reflects simply the reactions of one excited state. This perturbation is independent of the measuring technique, whether it be flash spectroscopy or quenching. Second, if the two excited chromophores have significantly different intrinsic lifetimes, apparent rates of their bimolecular reactions need not be linear in substrate concentration if each excited chromophore reacts with the added substrate. This perturbation is independent of the exact phenomenon being studied (quenching, sensitization, photoreduction, dimerization, cycloaddition, etc.).

$$(18) \epsilon_A/\epsilon_B = 2.3; k_{-t}[B]\tau_A \approx 0.7; k_i[A]\tau_B = 0.25.$$

Peter J. Wagner,\* Takayuki Nakahira

Department of Chemistry, Michigan State University  
East Lansing, Michigan 48823

Received January 19, 1974

## Nuclear Magnetic Resonance Spectral Studies. VIII. Titanium Tetrachloride as a Shift Reagent<sup>1</sup>

Sir:

Titanium tetrachloride is known to complex with polar functional groups, such as ether, ketone, and ester.<sup>2-4</sup> Since such complexing must affect the chemical shifts of neighboring nuclei, we have studied the effect of this easily available chemical on the nmr spectra of a variety of organic compounds. We wish to report that titanium tetrachloride induced shifts in pmr and cmr spectra can provide useful information for the elucidation of structure. Currently several lanthanide shift reagents are extensively used for the simplification of nmr spectra.<sup>5-8</sup>

We have observed that the addition of titanium tetrachloride to a solution of alcohols, ethers, ketones, esters, acids, amides, and nitriles causes downfield

(1) For Part VII see A. K. Bose and R. J. Brambilla, Proceedings of the 1st International Conference on Stable Isotopes in Chemistry, Biology and Medicine, Argonne, Ill., May 1973, p 431.

(2) P. M. Hamilton, R. McBeth, W. Bekebrede, and H. H. Sisler, *J. Amer. Chem. Soc.*, **75**, 2881 (1953).

(3) F. Evard, *Compt. R. Acad. Sci.*, **196**, 2007 (1933).

(4) O. A. Osipov, Yu. A. Lysenko, and R. E. Akopov, *Zh. Obshch. Khim.*, **25**, 249 (1955) [*Chem. Abstr.*, **48**, 8104a (1954); **49**, 9368g (1955)]; Yu. A. Lysenko, *J. Gen. Chem. USSR* **26**, 3297 (1956); E. Rivet, R. Aubin, and R. Rivest, *Can. J. Chem.*, **39**, 2343 (1961).

(5) C. C. Hincley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(6) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).

(7) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(8) Jacques Reuben, *J. Amer. Chem. Soc.*, **95**, 3534 (1973).

shifts of protons in the vicinity of the functional group; the shift increases with increasing amounts of the shift reagent. The maximum shifts observed upon addition of titanium tetrachloride to representative compounds are shown in Table I. It can be seen that the magnitude

Table I. Titanium Tetrachloride Induced Shift<sup>a</sup>

| Compound<br>(CDCl <sub>3</sub> solution)                        | Downfield shift (ppm)                              |                  |                   |
|---|--|------------------|-------------------|
|   | $\alpha$ -protons                                  | $\beta$ -protons | $\gamma$ -protons |
| CH <sub>3</sub> CH <sub>2</sub> OH                              | 1.03   | 0.37             |                   |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH              | 1.05   | 0.37             | 0.15              |
| (CH <sub>3</sub> ) <sub>2</sub> CHOH                            | 1.03   | 0.38             |                   |
| (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O               | 0.80   | 0.30             |                   |
| (CH <sub>3</sub> ) <sub>2</sub> CO                              | 0.54   |                  |                   |
| (CH <sub>3</sub> CH <sub>2</sub> )CO                            | 0.56   | 0.30             |                   |
| CH <sub>3</sub> CO <sub>2</sub> H                               | 0.40   |                  |                   |
| CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> | 0.45 (CH <sub>2</sub> )<br>0.50 (CH <sub>3</sub> ) | 0.20             |                   |
| CH <sub>3</sub> CN  | 0.25   |                  |                   |
| CH <sub>3</sub> CH <sub>2</sub> CN                              | 0.45   | 0.19             |                   |

<sup>a</sup> An excess of TiCl<sub>4</sub> (~0.55 equiv) was used. Shifts reached a maximum value when 0.5 equiv of TiCl<sub>4</sub> was added; further addition had no effect. Spectra were recorded on a Varian A-60-A spectrometer with TMS as the internal standard.

of the shift decreases with the distance from the functional group. For example, in the pmr spectrum of ethyl butyrate (Figure 1), the methyl signal of the ethyl group could be recognized by its larger shift than the other methyl group upon addition of TiCl<sub>4</sub>. This was verified by decoupling studies.

A series of shift measurements were made on a few monofunctional compounds by adding incremental amounts of titanium tetrachloride. When the induced shift was plotted against the relative molar ratio of the shift reagent and the substrate, a linear relationship was observed. The slope of this line was determined by a standard least-squares computer analysis.<sup>9</sup> The "sensitivity" (defined here as extrapolated value of the shift to correspond to equimolar amounts of reagent and substrate) of various protons is listed in Table II. It

Table II. "Sensitivity"<sup>a</sup> to Titanium Tetrachloride

| Compound<br>(CDCl <sub>3</sub> solution)                          | Downfield shift (ppm)                                   |                  |                   |
|---|---|------------------|-------------------|
|   | $\alpha$ -protons                                       | $\beta$ -protons | $\gamma$ -protons |
| (CH <sub>3</sub> ) <sub>2</sub> CO                                | 1.11  |                  |                   |
| CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>                 | 1.85 (CH <sub>3</sub> )<br>1.47 (CH <sub>2</sub> )      | 0.60             |                   |
| (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CO                | 1.16  | 0.49             |                   |
| [(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> CO              | 1.46  | 0.51             |                   |
| (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O                 | 1.27  | 0.38             |                   |
| (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O | 0.76  | 0.30             | 0.05              |
| CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>                   | 1.45 (CH <sub>3</sub> CO-)<br>1.01 (-OCH <sub>3</sub> ) |                  |                   |
| CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>   | 1.26 (CH <sub>3</sub> CO-)<br>0.86 (-OCH <sub>2</sub> ) | 0.41             |                   |

<sup>a</sup> Extrapolated value of the shift to correspond to equimolar amounts of reagent and substrate (see text).

can be seen that the "sensitivity" to titanium tetrachloride follows the order of alcohol > ether > ester > nitrile. In most cases, the maximum shift observed was about one-half of the "sensitivity" values in Table II

(9) J. W. ApSimon, H. Beierbeck, and A. Fruchier, *J. Amer. Chem. Soc.*, **95**, 939 (1973).

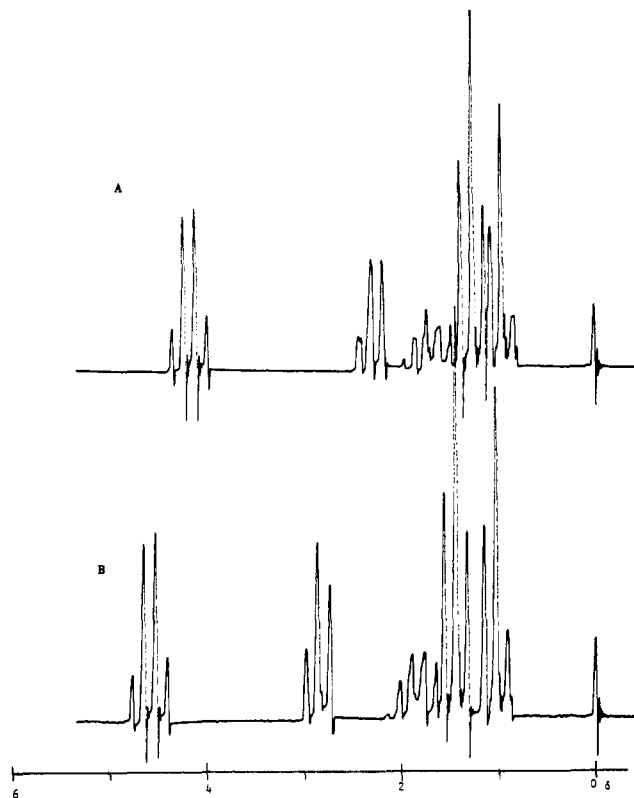


Figure 1. Pmr spectrum of ethyl butyrate before addition of  $\text{TiCl}_4$  (A) and after addition of  $\text{TiCl}_4$  (0.7 equiv) (B).

indicating that a 1:2 complex can be formed between titanium tetrachloride and the organic substrate.

Titanium tetrachloride can serve as a convenient shift reagent although the shifts are not very large. Thus, addition of titanium tetrachloride (in small amounts to prevent precipitation) to 3-cholestanone clearly separates ( $\Delta = -0.55$  ppm) the C-2 and C-4 protons from the large proton envelope and moves the 19-methyl group slightly downfield ( $\Delta = -0.06$  ppm). In case of camphor, correct assignments<sup>10</sup> for the protons at C-3 and the methyl groups could be made easily (see Figure 2).

Titanium tetrachloride produces appreciable shifts in cmr spectra (see Table III); the shifts can be either upfield or downfield. Comparison of shifts induced in the cmr spectrum of camphor by  $\text{Eu}(\text{fod})_3$  and by  $\text{TiCl}_4$  are markedly different in magnitude and direc-

Table III. Shifts Induced in the Nmr Spectra of *trans*-1,4-Diphenyl-3-methyl-2-azetidione

| Reagent                     | Shift <sup>c</sup> (ppm) | CO    | C <sub>3</sub> -H | C <sub>4</sub> -H | CH <sub>3</sub> |
|-----------------------------|--------------------------|-------|-------------------|-------------------|-----------------|
| $\text{TiCl}_4^a$           | Cmr spectrum             | -5.50 | +1.19             | -1.94             | -0.76           |
| $\text{Eu}(\text{fod})_3^b$ | Cmr spectrum             | -0.11 | -1.19             | -0.54             | -0.54           |
| $\text{TiCl}_4^d$           | Pmr spectrum             |       | -0.75             | -0.35             | -0.26           |

<sup>a</sup> A limited quantity ( $\sim 0.2$  equiv) added. <sup>b</sup> 25% by weight added. <sup>c</sup> Shift to lower magnetic field is designated as negative. <sup>d</sup> Excess reagent (0.52 equiv) added.

(10) R. Tori, Y. Hamashima, and A. Takamizawa, *Chem. Pharm. Bull.*, **12**, 924 (1964); *Chem. Ind. (London)*, 3179 (1965).

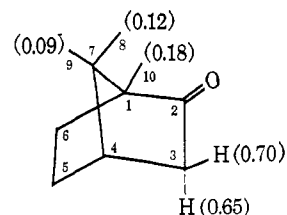


Figure 2. Shifts produced in the pmr spectrum of camphor in  $\text{CDCl}_3$  solution upon addition of an excess of  $\text{TiCl}_4$  (0.55 equiv) in  $\text{CDCl}_3$ ; the numbers in parentheses denote downfield shifts in ppm. Shifts reached a maximum value when 0.5 equiv of  $\text{TiCl}_4$  was added; further addition had no effect.

tion of shift. It is obvious that steric and distance factors affect differently the contribution of these two shift reagents. Further investigation is in progress on the effect of  $\text{TiCl}_4$  on cmr spectra. Studies on the nmr spectra of various  $\beta$ -lactams using titanium tetrachloride as a shift reagent will be reported elsewhere.

As a shift reagent, titanium tetrachloride has some advantages over lanthanides: it is much cheaper and more readily available in many laboratories than lanthanide shift reagents, it does not shift the signals due to TMS,<sup>11</sup>  $\text{CHCl}_3$ , or  $\text{CH}_2\text{Cl}_2$ , there is little broadening of signals, it does not contribute any signals to the pmr or cmr spectrum, and the substrate can be recovered in many cases by adding an excess of water and extracting with a suitable organic solvent (see below for some exceptions).

Some of the disadvantages of titanium tetrachloride are that the shifts are smaller than those produced by lanthanides, structural information can be obtained only in the immediate neighborhood of a functional group, amines, tertiary alcohols, and polyfunctional molecules produce complexes with limited solubility, and allylic, benzylic, and other reactive alcohols undergo slow chemical reaction forming chlorides. Titanium tetrabromide and tetraiodide are not sufficiently soluble in chlorinated solvents to be useful. Titanium tetrachloride which is very sensitive to moisture is best used as a solution (25–30% by volume) in  $\text{CDCl}_3$ .

**Acknowledgment.** The authors are grateful to Stevens Institute of Technology for the support of this research and the Hayden Foundation for a generous grant toward the purchase of a Bruker HX-90 spectrometer.

(11)  $\text{TiCl}_4$  is reported to react with hexamethyldisilane (HMDS) to give  $\text{Me}_2\text{SiCl}_2$ : R. C. Paul, A. Arneja, and S. P. Narula, *Inorg. Nucl. Chem. Lett.*, **5**, 1013 (1969).

(12) Undergraduate research participant supported by the "Work-Study Program" of the Department of Health, Education and Welfare.

Ajay K. Bose,\* P. R. Srinivasan, George Trainor<sup>12</sup>  
Department of Chemistry and Chemical Engineering  
Stevens Institute of Technology  
Hoboken, New Jersey 07030  
Received January 11, 1974

### Photodissociation of $\text{Fe}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_5^-$ in the Gas Phase

Sir:

The interaction of light with gas-phase anions usually leads to the detachment of electrons. The wavelength