

Figure 1. Pmr spectrum of ethyl butyrate before addition of TiCl_4 (A) and after addition of 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 assignments¹⁰ 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 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 ^c (ppm)	CO	C ₃ -H	C ₄ -H	CH ₃
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
TiCl_4^d	Pmr spectrum		-0.75	-0.35	-0.26

^a A limited quantity (~ 0.2 equiv) added. ^b 25% by weight added. ^c Shift to lower magnetic field is designated as negative. ^d 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).

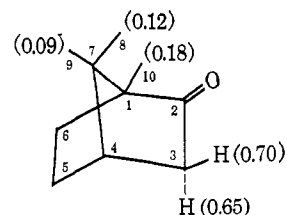


Figure 2. Shifts produced in the pmr spectrum of camphor in CDCl_3 solution upon addition of an excess of TiCl_4 (0.55 equiv) in CDCl_3 ; the numbers in parentheses denote downfield shifts in ppm. Shifts reached a maximum value when 0.5 equiv of TiCl_4 was added; further addition had no effect.

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 TiCl_4 on cmr spectra. Studies on the nmr spectra of various β -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,¹¹ CHCl_3 , or CH_2Cl_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 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) TiCl_4 is reported to react with hexamethyldisilane (HMDS) to give Me_3SiCl : 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.

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Photodissociation of $\text{Fe}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_3^-$ in the Gas Phase

Sir:

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

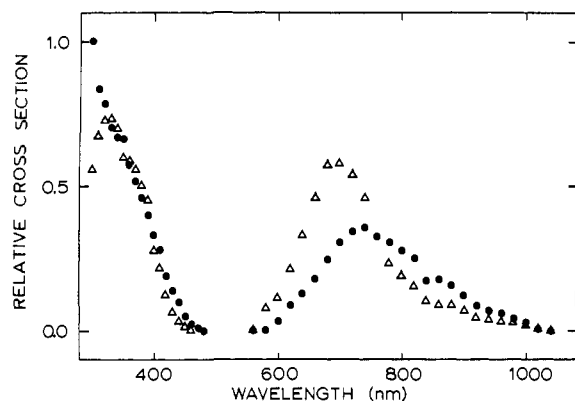


Figure 1. Relative photodissociation cross sections. (●) $\text{Fe}(\text{CO})_4^-$ disappearance: data below 550 nm, 9.6 nm band width (fwhm), average of eight runs; data above 550 nm, 39.6 nm fwhm, seven runs, multiplied $\times 10$. (Δ) $\text{Fe}(\text{CO})_3^-$ appearance: data below 550 nm, 14.1 nm fwhm, nine runs; data above 550 nm, 59.1 nm fwhm, four runs, multiplied $\times 10$. The $\text{Fe}(\text{CO})_3^-$ and $\text{Fe}(\text{CO})_4^-$ curves are normalized relatively so as to minimize the variance. All standard deviations $\sim \pm 10\%$.

dependence of such processes gives photodetachment spectra and often allows the estimation of the electron affinities of the corresponding neutral species.^{1,2} Our recent extension of these methods to complex molecular anions has revealed unusual photodetachment cross sections, but no new photoprocesses were apparent.^{3,4} We now report evidence for the *photodissociation* of $\text{Fe}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_3^-$. Moseley, Bennett, and Peterson⁵ have recently observed photodissociation of CO_3^- . We believe that these two observations constitute the first clear examples of negative ion photochemistry in the gas phase.⁶ The interpretation of such data offers the possibility of determining ligand binding energies as well as state densities in these negative ions.

Iron pentacarbonyl (Alfa) was filtered and stored excluding light and moisture. An ion cyclotron resonance spectrometer was used to generate, trap, and detect negative ions. High trapping voltages (2.0 V) were used with low analyzer and moderate source drift voltages. The $\text{Fe}(\text{CO})_5$ pressure⁷ was varied between 2×10^{-7} and 2×10^{-6} Torr. At low electron energies the dominant negative ion was $\text{Fe}(\text{CO})_4^-$ with some $\text{Fe}(\text{CO})_3^-$ present. At higher energies the relative amount of $\text{Fe}(\text{CO})_3^-$ decreased to zero. Ion ejection experiments⁸ demonstrated that $\text{Fe}(\text{CO})_4^-$ was not a precursor of $\text{Fe}(\text{CO})_3^-$ in the absence of light. No impurities were detected in the negative ion spectrum.

(1) L. M. Branscomb in "Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press, New York, N. Y., 1962, pp 100-140; S. J. Smith, *Methods Exp. Phys.*, **7a**, 179 (1968).

(2) See K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 5993 (1972), and references therein for some previous work from these laboratories.

(3) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Chem. Phys.*, **59**, 5068 (1973).

(4) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *Chem. Phys. Lett.*, in press.

(5) J. T. Moseley, R. A. Bennett, and J. R. Peterson, submitted to *Chem. Phys. Lett.*, personal communication.

(6) Also, see (a) E. E. Ferguson, F. C. Fehsenfeld, and A. V. Phelps, *J. Chem. Phys.*, **59**, 1565 (1973); (b) J. A. Burt, *ibid.*, **59**, 1567 (1973).

(7) Pressure was recorded at the Vac-Ion pump; the error for estimating the actual pressure in the cell may be as large as a factor of 2.

(8) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

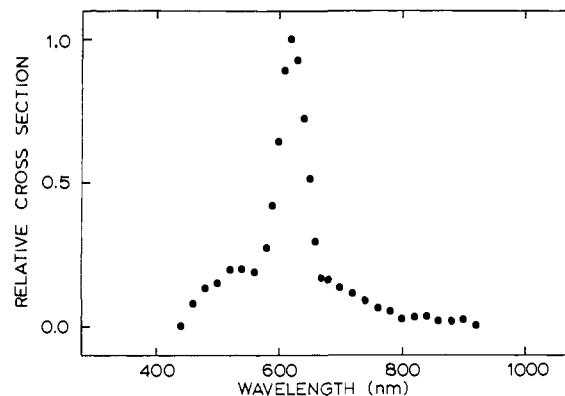


Figure 2. (●) $\text{Fe}(\text{CO})_2^-$ relative photoappearance cross section, average of three runs, 39.6 nm fwhm. Standard deviations $\sim \pm 10\%$. Cross section remains at zero to well below 400 nm.

Details of the spectrometer operation and the light source together with a description of the data collection and analysis have been reported previously.⁹ Figure 1 presents the results for the disappearance of $\text{Fe}(\text{CO})_4^-$ and the concomitant appearance of $\text{Fe}(\text{CO})_3^-$. In these experiments the average maximum signal decrease for $\text{Fe}(\text{CO})_4^-$ was 8.4%. The average maximum signal increase for $\text{Fe}(\text{CO})_3^-$ (relative to the average total $\text{Fe}(\text{CO})_4^-$ signal) was somewhat less, $\sim 4.5\%$. To facilitate comparison, data for $\text{Fe}(\text{CO})_3^-$ are normalized so as to minimize the total variance between the $\text{Fe}(\text{CO})_4^-$ relative disappearance cross section and the $\text{Fe}(\text{CO})_3^-$ relative appearance cross section.¹⁰

Photodissociation of $\text{Fe}(\text{CO})_4^-$ to $\text{Fe}(\text{CO})_3^-$ is suggested by the close similarity between the two cross sections. Several experiments further substantiate this conclusion. (1) When the light was turned on, $\text{Fe}(\text{CO})_3^-$ appeared even when only $\text{Fe}(\text{CO})_4^-$ was initially present. (2) Partial ejection of $\text{Fe}(\text{CO})_4^-$ resulted in a corresponding decrease in the amount of $\text{Fe}(\text{CO})_3^-$ produced during irradiation. (3) Higher aggregates¹² such as $\text{Fe}_2(\text{CO})_6^-$ are not photosources of $\text{Fe}(\text{CO})_3^-$. The $\text{Fe}_2(\text{CO})_6^-$ does appear to produce $\text{Fe}_2(\text{CO})_5^-$ and $\text{Fe}_2(\text{CO})_4^-$, however, when irradiated. (4) The obvious loss mechanism for irradiated $\text{Fe}(\text{CO})_4^-$, photodetachment of an electron, does not occur significantly as evidenced by our inability to detect detached electrons.¹³

Experiments with plane polarized light demonstrate that, while the orientation of the optical E vector was immaterial with regard to the disappearance of $\text{Fe}(\text{CO})_4^-$, the $\text{Fe}(\text{CO})_3^-$ appearance was preferentially enhanced when the optical E vector was parallel to the magnetic field.¹⁴ This implies a nonisotropic scattering of the $\text{Fe}(\text{CO})_3^-$ and CO in the photodissociation

(9) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 1132 (1972).

(10) The difference between the magnitudes of loss of $\text{Fe}(\text{CO})_4^-$ and appearance of $\text{Fe}(\text{CO})_3^-$ may be due to the following, among others: (a) loss of product ions owing to their velocity increase,¹¹ (b) rapid chemical reactions of $\text{Fe}(\text{CO})_3^-$, and (c) photodissociation of $\text{Fe}(\text{CO})_3^-$. (See text.)

(11) G. E. Busch and K. R. Wilson, *J. Chem. Phys.*, **56**, 3626 (1972).

(12) R. C. Dunbar, J. F. Ennever, and J. P. Fackler, Jr., *Inorg. Chem.*, **12**, 2734 (1973). $\text{Fe}(\text{CO})_4^-$ does not react with $\text{Fe}(\text{CO})_5$ to any significant extent.

(13) We have established that detached electrons can be detected as a result of their reactions with a variety of neutrals including CCl_4 . For example, CCl_4 produces Cl^- . A. A. Christodoulides and L. G. Christophorou, *J. Chem. Phys.*, **54**, 4691 (1971).

(14) For a previous ICR-polarized light experiment, see R. C. Dunbar and J. M. Kramer, *J. Chem. Phys.*, **58**, 1266 (1973).

process.¹⁵ This result implies that the product ion must be formed with appreciable kinetic energy,¹¹ and it is consistent with an expected¹⁶ nontetrahedral geometry for $\text{Fe}(\text{CO})_4^-$.¹⁷

The $\text{Fe}(\text{CO})_3^-$ can itself photodissociate to yield $\text{Fe}(\text{CO})_2^-$ (Figure 2). The average maximum $\text{Fe}(\text{CO})_2^-$: $\text{Fe}(\text{CO})_3^-$ intensity ratio was 3%. No photoproduction of $\text{Fe}(\text{CO})_2^-$ occurs if $\text{Fe}(\text{CO})_3^-$ is continuously ejected; the cross section is unaffected if $\text{Fe}(\text{CO})_4^-$ is ejected. Filter studies confirm that the disappearance of $\text{Fe}(\text{CO})_3^-$, with $\text{Fe}(\text{CO})_4^-$ being partially ejected, parallels the appearance of $\text{Fe}(\text{CO})_2^-$; signal/noise considerations prevented monochromator data for the disappearance of $\text{Fe}(\text{CO})_3^-$ from being taken.

In accord with previous work,¹² we find that $\text{Fe}(\text{CO})_3^-$ appears to be more reactive than $\text{Fe}(\text{CO})_4^-$. For example, $\text{Fe}(\text{CO})_3^-$ condenses with $\text{Fe}(\text{CO})_3$ to give $\text{Fe}_2(\text{CO})_6^-$; increases in $\text{Fe}_2(\text{CO})_6^-$ (due to newly formed $\text{Fe}(\text{CO})_3^-$) were observed upon irradiation with light. In the presence of SF_6 the usual photodissociation curve for $\text{Fe}(\text{CO})_4^-$ was observed but no $\text{Fe}(\text{CO})_3^-$ was detected. Instead, new ions corresponding to $\text{Fe}(\text{CO})_2\text{F}_2^-$, $\text{Fe}(\text{CO})_2\text{F}^-$, and $\text{Fe}(\text{CO})_2\text{F}_2^-$ were detected upon irradiation with light. Further investigations of the chemistry of $\text{Fe}(\text{CO})_3^-$ are planned.

Acknowledgments. We thank Robert G. Komoto and Professor Richard Zare for helpful discussions and John V. Garcia for technical assistance. This work was supported by the National Science Foundation (GP-37044-X) and the Center for Materials Research, Stanford University.

(15) Because the potentials on the side (trapping) plates are greater than those on the top and bottom (analyzer) plates, it is easier to lose product ions from the cell when they are ejected preferentially in the vertical direction. The disappearance of reactant has no orientational dependence; thus the effect cannot be a result of anisotropic distribution of reactant ions in the cell or anisotropic photon flux. Consequently, we can associate a preferential direction of dissociation with a specific orientation of the optical E vector.

(16) Expected, since if tetrahedral, $\text{Fe}(\text{CO})_4^-$ would undergo Jahn-Teller distortion. $\text{Fe}(\text{CO})_4^{2-}$ is tetrahedral: W. F. Edgell, *et al.*, *J. Amer. Chem. Soc.*, **87**, 3080 (1965); H. Stammreich, *et al.*, *J. Chem. Phys.*, **32**, 1482 (1960). $\text{Fe}(\text{CO})_4$ is not tetrahedral: M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973).

(17) A tetrahedral molecule would be expected to show no anisotropy: For example, see C. Jonah, *J. Chem. Phys.*, **55**, 1915 (1971); R. N. Zare, *Mol. Photochem.*, **4**, 1 (1972); G. E. Busch and K. R. Wilson, *J. Chem. Phys.*, **56**, 3638 (1972).

(18) National Science Foundation Predoctoral Fellow.

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A Novel Ion-Molecule Reaction Involving Cleavage of the Carbonyl Bond in Ketones and Aldehydes¹

Sir:

In this communication we report a unique type of reaction which we have observed between CF_3^+ , C_2F_5^+ , or CCl_3^+ and a series of organic compounds containing a carbonyl functional group. Observation of this reaction is one of the early results of a series of experiments we have initiated in which the reactions of halo-

(1) This work was partially supported by the U. S. Atomic Energy Commission.

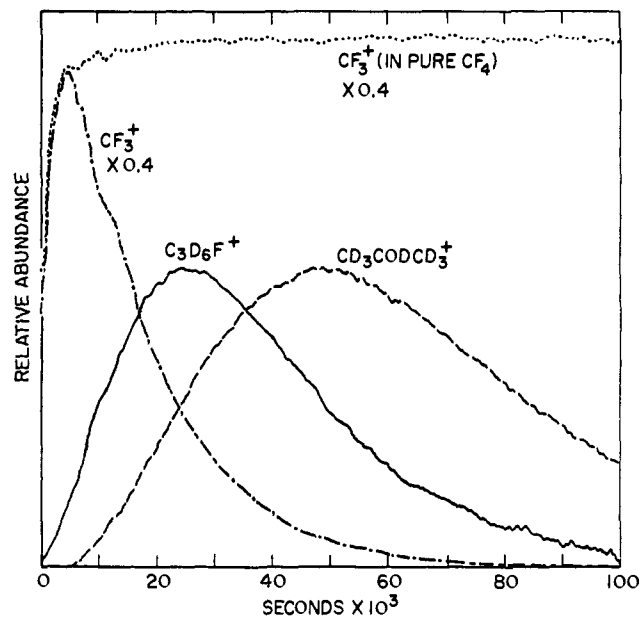


Figure 1. Relative abundances of ions formed in a CF_4 - CD_3 - COCD_3 (1:0.028) mixture as a function of time at a total pressure of 7.0×10^{-6} Torr and the abundance of CF_3^+ in the absence of additives under the same conditions. The $\text{CD}_3\text{CODCD}_3^+$ ion disappears because of further reaction with CD_3COCD_3 to form the $(\text{CD}_3\text{COCD}_3)_2\text{D}^+$ ion.

carbon ions with various types of organic molecules are investigated.²

All experiments were carried out in a pulsed ion cyclotron resonance (icr) mass spectrometer^{2,3} in which relative abundances of reactant and product ions can be followed as a function of time after an initial ion formation pulse several milliseconds in duration. Mixtures containing 2-5% of a carbonyl compound in CF_4 , C_2F_6 , or CCl_4 were admitted to the icr instrument at pressures of 10^{-6} - 10^{-5} Torr. In these compounds, a pulse of 40 eV electrons results in the formation of CF_3^+ (in CF_4), CF_3^+ and C_2F_5^+ (in C_2F_6), and CCl_3^+ (in CCl_4) as the predominant primary ions;⁴ these ions are all unreactive with the respective parent compounds (see Figure 1). The observed decay of parent ions and growth of product ions as a function of time gave information about reaction mechanisms and allowed determination of reaction rate constants with an accuracy of $\pm 10\%$. In addition, all product ions were unambiguously traced to their particular precursor ion(s) through use of the technique of icr double resonance ejection.⁵

(2) J. R. Eyler, P. Ausloos, and S. G. Lias, to be submitted for publication.

(3) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971).

(4) When CF_4 , C_2F_6 , or CCl_4 are admitted to the instrument in the absence of additives, small fragment ions such as CF_2^+ (in CF_4) or CCl_2^+ (in CCl_4) are formed initially along with the reactant ions of interest. However, these smaller ions react rapidly with the respective parent compounds, and in the pressure range used in these experiments are essentially absent after about $5-10 \times 10^{-3}$ sec. It should be pointed out that the use of high dilution mixtures for the investigation of these reactions (a technique similar to that called "chemical ionization mass spectrometry") not only allows us to ignore possible interactions with minor fragment ions but also ensures that the reactant ions undergo a sufficient number of unreactive collisions that those ions which react have attained thermal energies. This conclusion is supported by the fact that changes in mixture composition or pressure have no effect on the rates or modes of reaction observed.

(5) W. T. Huntress, Jr., and R. F. Pinizzotto, Jr., *J. Chem. Phys.*, **59**, 4742 (1973).