

ments with alkyl polygermanes and polystannanes show that they also appear to form CT complexes with TCNE. Work on these and other organometallic donors is in progress.

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Valery F. Traven,¹² Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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Intermolecular Donation of a σ -Electron from Group IVb Catenates to Tetracyanoethylene. Evidence of Electron Paramagnetic Resonance and Charge-Transfer Spectra

Sir:

During the course of the study on σ - π conjugation in arylpolysilanes,^{1,2} we have found that σ electrons of low ionization energy, such as of the Si-Si and Ge-Ge bonds, can be donated to certain π acceptors such as tetracyanoethylene (TCNE). For example, permethylpolysilanes, $\text{Me}(\text{SiMe}_2)_n\text{Me}$ ($n \geq 2$), form charge-transfer complexes with TCNE in dichloromethane. Such complexes were identified by both photoinduced epr signals of TCNE anion radicals and characteristic charge-transfer bands in the visible region. Although $\pi \rightarrow \pi$ or $n \rightarrow \pi$ electron donor-acceptor interactions have been well known,³ relatively few examples of σ donors are found in the literature.^{4,5} This fact appears to be related to the high ionization potentials of σ electrons, relative to n and π electrons, in most molecules.

Solutions (ca. 0.1 M) of TCNE and permethylpolysilane (ca. 0.1 M) in dichloromethane were placed in a Pyrex tube, degassed as thoroughly as possible by freeze-thaw cycles, and sealed. The samples were cooled to -60 to -70° and examined for a spontaneous epr signals using a Varian E 12 spectrometer. No signal was observed without irradiation;⁶ however, when the sample was irradiated with a focused 500-W super-high-pressure mercury lamp, an immediate and strong nine-line epr photosignal of the TCNE radical anion was observed. The splitting constant ($a_N = 1.556$ G) agreed with that recorded for the sodium salt in tetrahydrofuran ($a_N = 1.56 \pm 0.02$ G).⁷ The epr photosignal reached a maximum within 3 sec after the ultraviolet light was turned on and decayed to zero during periods of prolonged irradiation. Although the counteraction (or a radical cation) is not identified,⁸

(1) H. Sakurai, S. Tasaka, and M. Kira, *J. Amer. Chem. Soc.*, **94**, 9285 (1972).

(2) H. Sakurai and M. Kira, *J. Amer. Chem. Soc.*, submitted for publication.

(3) (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969; (c) R. S. Mulliken and W. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969.

(4) S. H. Hastings, J. L. Franklin, J. C. Schilker, and F. A. Matsen, *J. Amer. Chem. Soc.*, **75**, 2900 (1953).

(5) R. R. McLean, D. W. A. Sharp, and J. M. Winfield, *Chem. Commun.*, 452 (1970); *J. Chem. Soc., Dalton Trans.*, 676 (1972).

(6) In some cases weak dark signals were observed, but unidentified.

(7) W. D. Phillips, J. C. Rowell, and S. I. Weissmann, *J. Chem. Phys.*, **33**, 626 (1960).

(8) After the ultraviolet light was turned off, the epr signal disappeared immediately. Therefore, there exists free radicals or radical cations which can combine with TCNE.

the TCNE radical anion should arise from charge-transfer interaction with polysilanes.

The intensities of photosignals depend upon the length of the polysilane chain: the weakest signal was observed for hexamethyldisilane and the strongest signals were observed for the longer polysilanes. Therefore, higher polysilanes form charge-transfer complexes more easily. Tetramethylsilane did not give the photosignal under the same experimental conditions.

After Lagercrantz and Yhland used epr to demonstrate the photoinduced transfer of an electron from donors to acceptors in solution,⁹ several workers have reported on the existence of epr signals arising from donor-acceptor interactions, both in the presence and absence of irradiation.¹⁰⁻¹² Many π donors, such as benzene and its derivatives, and n donors, such as THF and amines, give rise to epr signals involving TCNE radical anions in the presence and/or absence of irradiation. However, the photoinduced transfer of an electron from compounds with only a σ framework to a π acceptor has not been known to date.

The donor properties of permethylpolysilanes have been further demonstrated by appearance of charge-transfer bands when permethylpolysilane and TCNE were dissolved in dichloromethane.¹³ Table I lists

Table I. Frequencies for Charge-Transfer Absorptions in Complexes of TCNE with Permethylpolysilanes, $\text{Me}(\text{SiMe}_2)_n\text{Me}$, in Dichloromethane at Room Temperature

n	ν_{max}		IP(EI), ^a eV	IP(PE), ^b eV
	cm^{-1}	eV		
2	24,000	2.97	8.00	8.69
3	21,100	2.61	7.53	8.19
4	19,600	2.43	7.29	7.98
5	18,400	2.28	7.11	(7.79) ^c

^a Reference 14. ^b Reference 15. ^c Calculated from the relationship between IP(EI) and IP(PE) for linear permethylpolysilane: $\text{IP(PE)} = 1.009 \text{ IP(EI)} + 0.613$ ($r = 0.999$).

the frequencies of band maxima and ionization potentials of polysilanes as determined by electron impact¹⁴ (EI) and photoelectron spectroscopic (PE) methods.¹⁵

Although charge transfer interactions between permethylpolysilanes and TCNE are weak, well-defined charge-transfer spectra were observed. Interestingly, a good linear relationship between charge-transfer frequencies and ionization potentials of the respective polysilanes was obtained.¹⁶

$$\nu_{\text{CT}} (\text{eV}) = (0.771) \text{IP(PE)} - 3.716 \quad (r = 0.999)$$

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(10) D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).

(11) F. E. Stewart and M. Eisner, *Mol. Phys.*, **12**, 173 (1967).

(12) N. S. Isaacs and J. Paxton, *Photochem. Photobiol.*, **11**, 137 (1970).

(13) V. F. Traven and R. West, *J. Amer. Chem. Soc.*, **95**, 6824 (1973), have observed similar charge-transfer complexing between permethylpolysilanes and TCNE in chloroform.

(14) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *J. Amer. Chem. Soc.*, **92**, 519 (1970).

(15) H. Bock and W. Ensslin, *Angew. Chem.*, **83**, 404 (1971).

(16) However, this linear relation has only a limited accuracy since unsymmetrical shapes of CT bands indicate overlapping multiple transitions. The separation of the two highest occupied molecular orbitals for decamethyltetrasilane is, for example, only 0.78 eV¹⁵ or 6300 cm^{-1} . Nevertheless, the relation is important enough to indicate the $\sigma \rightarrow \pi$ intermolecular charge transfer.

These facts, in combination, demonstrate that an electron transfer from a σ bond to π acceptor really occurred. Naturally, observation of these phenomena is not limited to polysilanes. Hexamethyldigermene showed a charge-transfer band maximum at 23,000 cm^{-1} and gave strong photosignals attributable to TCNE radical anions, whereas hexamethyldistannane underwent a spontaneous reaction with TCNE, presumably through a charge-transfer interaction, to give precipitates. Hydrocarbons with strained σ bonds are also expected to behave similarly.

Work on related spectroscopic, photochemical, and epr studies is in progress.

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Hideki Sakurai,* Mitsuo Kira, Takateru Uchida

Department of Chemistry, Faculty of Science
Tohoku University, Aobayama, Sendai, Japan

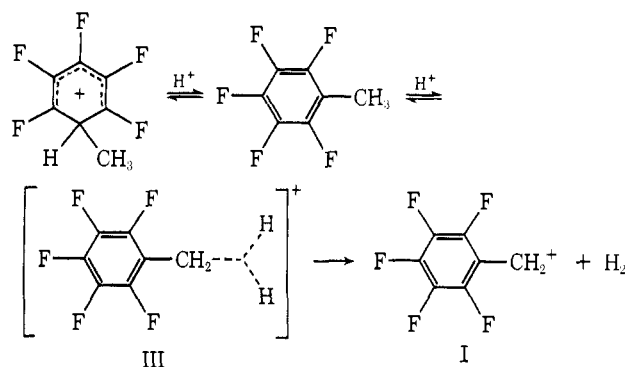
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Electrophilic Reactions at Single Bonds. VIII.¹ Side-Chain C-C and C-H σ -Bond Protolysis in Alkylbenzenes, Alkylpolyfluorobenzenes, Alkylbenzoic Acids, and Nitroalkylbenzenes. Competing σ - vs. π - and n-Donor Ability

Sir:

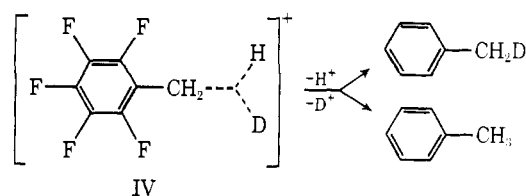
Evidence has been presented that alkanes undergo protolytic processes in superacids through the formation of pentacoordinated carbonium ions.² We now would like to report the protolytic behavior of some alkylbenzenes in superacids showing competing side-chain σ -bond protolysis with aromatic ring π protonation (as well as side-chain n-protonation in substituted alkylbenzenes).

When pentafluorotoluene is treated with $\text{HF-SbF}_5\text{-SO}_2\text{ClF}$ solution at -80° , the methyl protons display a temperature-dependent pmr singlet absorption at δ 2.60. It becomes broad when the temperature is raised (e.g., -30°) and sharpens when cooled back to -80° . The temperature dependence of the methyl absorption indicates hydrogen exchange with the superacid system. (Radical cation formation³ would also lead to the broadening, as it shortens the transverse relaxation time, T_2 ,⁴ but the ^{19}F nmr spectrum shows no such behavior.) The solution also shows an additional pmr singlet absorption at δ 9.60 which was found to be identical with that of the pentafluorobenzyl cation I. The ^{19}F nmr spectrum of ion I is also identical with that reported in our previous work.⁵ These results show that protonation of the $\text{C}_\alpha\text{-H}$ bond occurred leading through cleavage of III to I (and H_2). Pentafluoro-



toluene thus reacts like a substituted methane, *i.e.*, as a σ base. It, of course, is probable that initial protonation takes place on the π -electron system of the ring. The highly deactivated ring, however, is a poor π donor and ring π protonation leading to the benzenium ion II must be considered completely reversible (CH_3^+ and F^+ are both extremely poor leaving groups). Protonation at the nonbonded electron pairs of fluorine, due to the high electronegativity of fluorine, is also reversible. On the other hand, C-H protonation leads through cleavage of III to ion I. As the reaction is carried out at atmospheric pressure with H_2 escaping from the system, formation of I is not reversed.

We also found that pentafluorotoluene underwent hydrogen-deuterium exchange in $\text{DF-SbF}_5\text{-SO}_2\text{ClF}$ solution at -20° . The intensity of the methyl pmr absorption of pentafluorotoluene was gradually reduced and the peak split into a broad multiplet. Meanwhile, the intensity of acid pmr absorption was increased (some protic acid impurity giving rise to a low intensity peak at δ 10.2 was originally present in DF-SbF_5). Pentafluorotoluene, recovered on quenching of the solution with ice-water, showed extensive hydrogen-deuterium exchange (15% d_1 and 2% d_2) as analyzed by mass spectrometry. We suggest that the exchange reaction involves a three-center bound carbonium ion transition state IV similar to III.



Hydrogen abstraction through a linear transition state giving I and through its reaction with formed HD deuterated pentafluorotoluene could not explain, due to the very low concentration of HD in the system, the exchange results. These data explain the temperature-dependent pmr spectra of pentafluorotoluene in $\text{HF-SbF}_5\text{-SO}_2\text{ClF}$ solution.

In the case of secondary alkylbenzenes, such as isopropylbenzene and *sec*-butylbenzene, containing a tertiary benzylic C-H bond, side-chain C-H bond protolysis takes place in competition with ring protonation even without the presence of ring deactivating substituents. Thus, isopropylbenzene when treated with $\text{HF-SbF}_5\text{-SO}_2\text{ClF}$ solution at 0° gave 90% isopropylbenzenium ion V and 10% dimethylphenylcarbenium ion VI. The latter was observed as a singlet absorption at δ 4.1 and the characteristic aromatic ab-

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