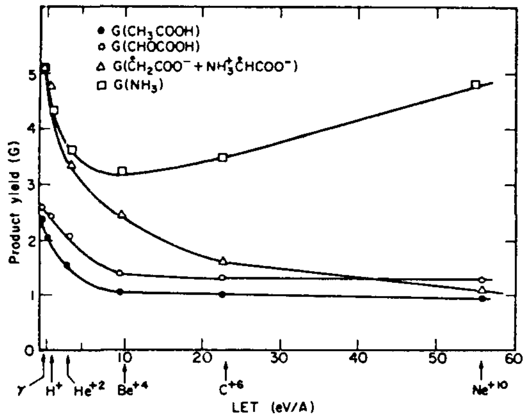

Figure 1. Product yields as a function of LET in the radiolysis of solid glycine: dose, 1.85×10^{20} eV/g; dose rate, 6×10^{18} eV/(g min). Radical yields are normalized to $G = 5.2$ as measured by Zimmer and Muller for the γ-radiolysis of solid glycine (ref 17).

Table I. Range and LET of Particles with Energies of 10 MeV per Nucleon

	H^+	He^{2+}	Be^{4+}	C^{6+}	Ne^{10+}
Particle energy (MeV)	10	40	90	120	200
Range (mg/cm^2)	110	110	75	45	35
LET (eV/Å)	0.7	2.8	10	23	56

The effects of LET on product yields from solid glycine are summarized in Figure 1. Over the LET range ~0.03 to ~10 eV/Å there is a steady decline in the yield of all products. However, at LET values above ~10 eV/Å the yields of acetic acid and glyoxylic acid become essentially independent of LET. Now it is well known[11-13] that fast charged particles lose energy to electrons of the absorbing media via (1) glancing collisions which have low energy loss (≤100 eV) per event and via (2) knock-on collisions which give rise to energetic secondary electrons. The glancing collisions form spurs which contain several ion pairs in close proximity.[12,14] With γ rays the spurs are widely separated and in polar media most of the electrons escape the parent positive ions. In the present system they become trapped via reaction 2. When the LET of the radiation is increased, the spurs begin to overlap and charge recombination, i.e.

$$(NH_3^+CH_2COO^-)^+ + e^- \rightarrow (NH_3^+CH_2COO^-)^{\ddagger} \quad (5)$$

can occur in competition with reaction 2. Hence, the product yields decrease as observed in Figure 1. Above ~10 eV/Å the spurs coalesce to form a track core which is surrounded by a sheath or penumbra of lower ionization.[13,15] The latter is formed by the energetic secondary electrons produced in knock-on collisions. It is in the penumbra that reaction 2 largely occurs. The finding that the yield of glyoxylic and acetic acids become independent of LET above ~10 eV/Å is consistent with the fact that the energy distribution of the secondary electrons ejected from the track core is the same for particles having the same velocty.[13] This is the case in the present study since all of the particles used have the same energy per nucleon. The fact that the limiting yield of glyoxylic and acetic acids at the higher LET values is essentially one-half the corresponding γ-ray values is in good accord with the theoretical conclusions that there is an equipartition of energy between knock-on collisions and glancing collisions.[12,13]

The free radical yield continues to decrease with increasing LET over the entire range studied. We conclude that reaction 3 occurs in part within the solid at the higher LET values.

The ammonia yield, which on the basis of the reaction scheme given in eq 1-4 should be equal to the sum $G(CH_3COOH) + G(CHOCOOH)$, does show an initial decrease with increasing LET but does not fall to the anticipated values of $G \simeq 2.5$. In fact, $G(NH_3)$ actually increases with LET above ~10 eV/Å. It is clear that processes in addition to those given by eq 1-4 become increasingly important at the higher LET values. We presume that such processes occur in or near the track core and may involve reactions of excited species formed in the recombination reaction 5.[16] The nature of this "core" chemistry is presently under investigation.

Acknowledgment. We are indebted to the staff of the 88-in. cyclotron for assistance in the irradiations. We also thank Dr. A. Chatterjee for helpful discussions on the theory of track structures.

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Received April 20, 1976

Formation of Highly Conducting Organic Salts by Photooxidation of Heterofulvalene π-Donors in Halocarbon Solutions

Sir:

The charge transfer salts of heterofulvalene-type π-donors such as tetrathiafulvalene (TTF)[1] and its derivatives[2] with tetracyanoquinodimethane and halogen acceptors are currently a major focus of organic solid state research because of their unusually high electrical conductivities.[3-5] In the course of crystal chemical studies of tetrathiafulvalinium–halide systems[3b,6] we have observed an unusual photooxidation reaction of TTF and related π-donors in halocarbon solvents such as CCl_4. The photooxidation reaction, which we report in this communication, provides a novel method for synthesizing[7] high conductivity π-donor/halide salts, and moreover, gives important insight into some of the factors governing the photooxidative stability of π-donors in such solvents.

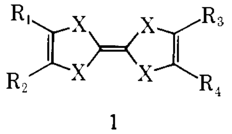

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Table I. Comparative Properties of Heterofulvalene π-Donors

Donor	$E_{1/2}$,[a] (eV)	I_p,[b] (eV)	$\epsilon(\lambda_{max}, nm)$[c]	K[d]	Conducting[e] mixed-valence salt (stoichiometry)	Hetero-fulvalene synthesis
TMTTF (**1**, X = S; $R_{1-4} = CH_3$)	0.27	(6.40)[f]	g(350)	*g*	(+) (0.71)	*k*
TTF (**1**, X = S; R_{1-4} = H)	0.33	6.95 (6.86)[f]	1.5×10^4 (330)	0.125	(+) (0.68)	*l*
TSeF (**1**, X = Se; R_{1-4} = H)	0.48	7.21	1.8×10^4 (320)	0.05	(+) (0.80)	*m*
Br_2TTF (**1**, X = S; $R_{1,3}$ = Br; $R_{2,4}$ = H; and $R_{1,4}$ = Br; $R_{2,3}$ = H)	0.59	—	*g* (300)	~0	(±) (*j*)	*n*
$(CO_2CH_3)_4TTF$ (**1**, X = S; R = CO_2CH_3)	0.80	—	*i*	0	(−)	*o*
$(CF_3)_4TTF$ (**1**, X = S; R = CF_3)	1.08	8.06[h] (7.95)[f]	*i*	0	(−)	*o*
$(CN)_4TTF$ (**1**, X = S; R = CN)	1.12	—	*i*	0	(−)	*p*

[a] First oxidation potential from peak in first wave of cyclic voltammetry in CH_3CN at Pt working electrode (5×10^{-5} M, 0.1 M Et_4NClO_4, 0.20 v/s sweep rate, volts vs. SCE). [b] Mass spectrometric gas phase ionization potential data unless otherwise noted (cf. ref 13). [c] Extinction coefficient (l. mol^{-1} cm^{-1}) at λ_{max} of donor–CCl_4 charge transfer band. [d] Equilibrium constant $(mol/l.)^{-1}$ for formation of donor–CCl_4 complex. [e] Formation of mixed-valence salt through uv irradiation of donor–CCl_4 solution denoted by (+), no reaction by (−), marginal reaction after extended irradiation by (±). Stoichiometry *n* in $(donor)Cl_n$ is given in parentheses. [f] Photoemission gas phase ionization potential data (R. Gleiter, M. Kobayashi, J. Spanget-Larsen, J. P. Ferraris, A. N. Bloch, K. Behgaard, and D. O. Cowan, to be submitted). [g] Extinction coefficient and *K* not determined. [h] Unpublished results of C. E. Klots and R. N. Compton, Oak Ridge National Laboratory. [i] No charge transfer band observed throughout accessible spectral region. [j] Not enough solid sample for analysis. [k] Cf. ref 2f. [l] Cf. ref 1. [m] Cf. ref 2c. [n] Prepared by R. Schumaker, IBM San Jose Research, unpublished. [o] H. D. Hartzler, *J. Am. Chem. Soc.*, **95,** 4379 (1973). [p] M. G. Miles, J. D. Wilson, D. J. Dahm, and J. H. Wagenknecht, *J. Chem. Soc., Chem., Commun.*, 751 (1974), and Z. Yoshida, T. Kawase, and S. Yoneda, *Tetrahedron Lett.*, 331 (1975).

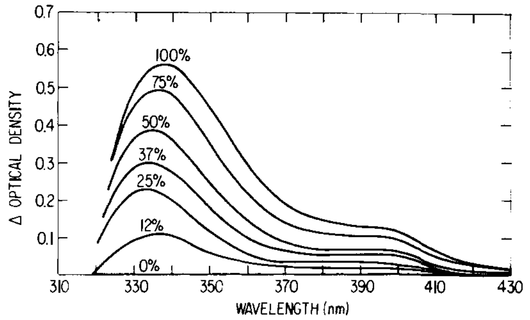

Figure 1. Optical density difference spectra for TTF solution (10^{-3} M) in CCl_4/hexane vs. TTF/hexane. Volume percents of CCl_4 in hexane are as shown.

The π-donors utilized in these experiments were synthesized in accordance with published procedures (see Table I) and purified by recrystallization, and, where possible, multiple gradient sublimation.[8] All other materials and solvents were AR grade and nitrogen purged prior to the experiments. Experiments were carried out under dry nitrogen atmosphere, with the exception of a series of experiments in which oxygen was bubbled into TTF/halocarbon solutions in the absence of light. No oxidation was observed in these control experiments, nor in controls carried out in uv light in the absence of CCl_4.

A solution of 2 mmol of TTF (2,2′-bis-1,3-dithiole[1]) in 100 ml of CCl_4 was irradiated with uv light (0.5 mW/cm^2) at 3650 Å. The yellow solution began to turn red almost immediately, with the appearance of a dark precipitate. After 3 h of illumination, 135 mg of precipitate were collected and recrystallized from absolute ethanol. Chemical analysis of the dark red needles corresponded to the composition $(TTF)Cl_{0.71}$, and its x-ray diffraction pattern could be completely indexed on the basis of a tetragonal unit cell with $a_0 = 11.12$ Å and $c_0 = 3.60$ Å. In all subsequent experiments the as-prepared or recrystallized tetragonal phase always formed within a composition range $(TTF)Cl_{0.68\pm0.03}$. This mixed-valence compound is highly conducting, exhibiting a powder compaction resistivity of 1.6 Ω cm. The identical experiment carried out with CBr_4 (CBr_4:TTF = 9:1) in hexane produced the analogous mixed-valence bromide phase, $(TTF)Br_{0.59\pm0.03}$. Although these stoichiometries appear to be unusual, complete studies of the TTF–halide systems indicate the existence of several mixed-valence $(TTF)Z_n$ (Z = halide) phases for $0.5 < n < 1.0$ in each system. The factors governing the composition, structure, and stability of these phases will be discussed separately.[3b,6] Briefly, in each system a mixed-valence $(TTF)Z_n$ phase occurs in the composition region $0.7 \leq n \leq 0.8$ exhibiting segregated stacking of $TTF^{0,+}$ and Z^- in *ordered*, sublattices.[3b-e] Below this range, structurally related phases begin to appear, typified by $(TTF)Cl_{0.68}$ and $(TTF)Br_{0.59}$, in which the halide sublattices are disordered.[9] These are the lowest members (i.e., those having the most TTF^0) of the possible mixed-valence phases, and it is not surprising that they should be precipitated upon photooxidation in halocarbon solution, since the uv irradiation is performed in the presence of excess TTF^0. In principle, use of solvents in which the mixed valence phases have greater solubilities should allow the direct photochemical preparation of compounds having higher TTF^+/TTF^0 ratios.

Photooxidative charge-transfer reactions in halocarbon solutions have been observed for ferrocene[10] and alkyl amines.[11] These reactions, which do not produce mixed-valence phases, have been shown to involve the initial formation of a weakly bound donor–haloalkane complex that can undergo dissociation through irradiation in its charge transfer band. Assuming a similar mechanism[10] for TTF-type π-donors leads to the equilibrium

$$TTF + CCl_4 \xrightarrow{K} (TTF)(CCl_4) \qquad (1)$$

$$(TTF)(CCl_4) \xrightarrow{h\nu_{ct}} (TTF^+)(CCl_4^-) \rightarrow TTF^+ + Cl^- + CCl_3 \qquad (2)$$

$$TTF^0 \text{ (excess)} + TTF^+ + Cl^- \rightarrow (TTF)Cl_{0.68}(s) \qquad (3)$$

where $h\nu_{ct}$ is the characteristic charge transfer band energy. Evidence for such a mechanism can be found in the uv-difference spectra of Figure 1 for TTF solutions in a solvent consisting of varying ratios of CCl_4/hexane. These spectra were obtained with a TTF–hexane solution reference and show a new absorption at 335 nm and a weaker shoulder at 400 nm which cannot be associated with oxidized forms of TTF. The apparent shift in the maximum of the main charge transfer band at 335 nm at higher concentrations of CCl_4 acceptor is due to unequal amounts of uncomplexed donor in the reference and sample solutions. We believe the main peak to be the primary charge transfer excitation of the complex between TTF and CCl_4. Although detailed kinetic studies would be required to elucidate the mechanism postulated in eq 1–3, the difference spectra provide evidence for the first step in such a process.

The equilibrium constants, K, for complex formation and extinction coefficients for absorption of complexes involving both TTF and TSeF (tetraselenofulvalene) donors were determined by the graphical iterative procedure of Rose and Drago,[12] and are collected in Table I. Also tabulated there are the results of irradiation experiments on CCl_4 solutions of other heterofulvalene donors having first oxidation potentials ($E_{1/2}$) in the range 0.27–1.12 V. In all cases for which $E_{1/2} \lesssim 0.60$, a charge transfer band was observed, and a mixed valence conducting donor–chloride salt was obtained upon uv irradiation. Apparently for larger $E_{1/2}$ compounds, the charge-transfer complex does not form (Table I) and photooxidative stabilization in the manner of reaction 2 is precluded in these cases. In this regard, it should be noted that TTF has a larger value of K than TSeF, which is a poorer donor by virtue of its higher $E_{1/2}$ and I_p values.[13] Taken together then, the results of Table I indicate that the tendency to form donor–halocarbon complexes, which can photodissociate to form mixed valence conducting salts, increases with donor strength. This suggests that charge transfer interactions are important to the stability of the complexes formed. The generality of this mechanism for other π-donor acceptor pairs is currently being investigated.

Acknowledgments. We wish to thank R. Thomas, R. B. Braccini, and V. V. Patel for their experimental assistance and Mr. B. L. Olson for carrying out the chemical analysis. We are also indebted to D. C. Green for measurements of $E_{1/2}$ values.

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Received February 11, 1976

Book Reviews

The Business of Science. By DAVID FISHLOCK (Science Editor, Financial Times). Halsted/Wiley, New York, N.Y. 1975. 189 pp. $14.95.

I had great difficulty in putting down this short and engaging book. It is very readable, the author being a skilled and intelligent journalist who for several years has brought to the pages of the *Financial Times* clear, undistorted accounts of scientific and developmental happenings.

The book deals with a few of the successes, and many of the failures, of large R&D programs as they encountered the market place. In the euphoria of the years immediately following World War II, industrial and governmental research budgets were burgeoning. "New patrons of science . . . were searching the land for ideas . . . into which they could invest their cash." But as Fishlock points out, the basic fallacy was the idea that "big research centres and crash programmes would hasten the pace of scientific understanding and discovery." Implicit, also, in that fallacy was the idea that all technological products would be financially profitable. In eight chapters which deal mainly with aviation, nuclear engineering, electronics, and drug manufacture, Fishlock shows how hazardous may be the consequences of that fallacy, no matter whether the patrons are governments or private enterprise.

From the viewpoint of the American reader, it is a little unfortunate that almost all of the case studies are drawn from British experiences and that many of the vehement (and costly) disputes which are recorded involve persons relatively little known on this side of the Atlantic. Nevertheless, the lessons taught by the case studies are clearly expounded and, without doubt, present much from which research workers and industrialists in the U.S. can learn.

Fishlock writes from a particular viewpoint—that of the journalist working for a financial paper. Even so, he is probably correct in his observation that most research "is predominantly a business operation, financed primarily for 'commercial' and not for cultural reasons. One can easily lose sight of this point when the academics stampede . . . [it is] at best an astonishingly successful technique, but at worst one that can be cripplingly expensive." Congressmen, bureaucrats, industrial investors, *and* research workers will find much to stimulate—and doubtless to irritate—them in this brief yet highly compact account of R&D in Britain.

Eric Hutchinson, *Stanford University*