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Relative Rates of Halogen Addition to Double and Triple Bonds. The Bromination of *trans*-Cinnamic and Phenylpropiolic Acids and Their Esters

Sir:

The difference in reactivity of olefinic and acetylenic double bonds in addition reactions has long been considered noteworthy and is important for a better understanding of the mechanisms of these reactions.[1,2] As a contribution to this problem, we wish to report data on the bromination of *trans*-cinnamic and phenylpropiolic acids, and their methyl esters, under well-defined kinetic conditions.

The 3-hexenes react about 3 × 10^5 times faster than 3-hexyne, and *trans*-1-phenylpropene 5000 times faster than phenylmethylacetylene, with bromine in acetic acid.[2] These and similar large differences in bromination and chlorination have usually been ascribed to the higher energy of the vinyl cation intermediates (bridged or open), as compared with the intermediates in olefinic halogenation.[3] In other addition reactions, e.g., in hydration, the differences are much reduced.

However, some of the data on which rate differences are based may not be free from ambiguities. In the presence of bromide ion some of the bromination reactions follow two-term rate expressions (see below). The two terms need to be sorted out, because they probably correspond to different mechanisms of addition, depending on whether the substrate is an olefin or an acetylene.

trans-Cinnamic acid and phenylpropiolic acid and their methyl esters were brominated under identical conditions in 75% aqueous acetic acid (by volume) in the presence of varying amounts of sodium bromide (0.02–0.5 M), and at a constant ionic strength (0.5 M, $NaClO_4$). Under these conditions the rate expression is $-\mathrm{d}(\mathrm{Br}_2)_\mathrm{T}/\mathrm{d}t = k_\mathrm{obsd}(\mathrm{Br}_2)_\mathrm{T}(\mathrm{A})$, where $(\mathrm{Br}_2)_\mathrm{T}$ is the titratable bromine, and A the substrate. In the presence of bromide ion the total rate of bromination can be expressed by eq 1.

$$-\mathrm{d}(\mathrm{Br}_2)_\mathrm{T}/\mathrm{d}t = k_2(\mathrm{Br}_2)_{free}(\mathrm{A}) + k_3(\mathrm{Br}_2)_{free}(\mathrm{Br}^-)(\mathrm{A}) \quad (1)$$

The second term is written as a bromide ion catalyzed reaction and involves a termolecular attack of bromine and bromide ion (Ad3), as first demonstrated by Pincock and Yates for bromination of acetylenes.[4] This interpretation of the second term also applies to acetylenic iodinations[5] and hydrochlorinations,[6] and is strongly supported by product composition.

However, the second term in eq 1 is indistinguishable kinetically from a reaction involving the tribromide ion, $k_{\mathrm{Br}_3^-}(\mathrm{Br}_3^-)(\mathrm{A})$, and $k_3K = k_{\mathrm{Br}_3^-}$, where K is the dissociation constant for the tribromide ion. In olefinic halogenation this term has usually been interpreted as an electrophilic attack by the tribromide ion, as first shown by Bartlett and Tarbell.[7] The second terms, therefore, refer to different mechanisms of halogenation and their magnitudes cannot be compared.[8] If one is interested in the relative rates of halogenation, one must compare the first terms only, which unambiguously represent an electrophilic attack by molecular bromine on the substrate ($\mathrm{Ad_E2}$).

The different rate constants can be obtained from the equation $k_\mathrm{obsd}(K + \mathrm{Br}^-)/K = k_2 + k_3(\mathrm{Br}^-)$, by plotting the term on the left against the bromide ion concentration. The rate constant k_2 is 1.97 ± 0.02 $M^{-1}\,s^{-1}$ for bromination of phenylpropiolic acid and (2.86 ± 0.08) × 10^{-1} $M^{-1}\,s^{-1}$ for bromination of *trans*-cinnamic acid. The acetylenic acid reacts about seven times faster than the olefinic acid. This, however, is not a true comparison. It is thought that the bromination of both of the acids proceeds through their respective anions, and K_a for phenylpropiolic acid in water is over 100 times greater than that for *trans*-cinnamic acid.[9] Hence more of the anionic acetylenic substrate will be present, which would account for its greater rate of reaction. But in the bromination of the respective methyl esters, k_2 is (4.75 ± 0.68) × 10^{-3} $M^{-1}\,s^{-1}$ for the bromination of methyl phenylpropiolate and (1.30 ± 0.04) × 10^{-1} $M^{-1}\,s^{-1}$ for that of methyl *trans*-cinnamate. The olefinic ester reacts 27 times faster than the acetylenic one.[10] Thus, the difference in relative reactivities of these unsaturated esters and acids has been greatly reduced when compared to the data on hydrocarbons quoted in the introduction. These results support the suggestion, first advanced by Robertson,[11] that the difference in reactivity of acetylenes and olefins in halogenation depends on the substituents attached to the unsaturated center, and that the halogenation of olefins is affected to a greater extent by the nature of the substituents than that of acetylenes.[1,12] The quoted reduction in the ratio to 5000, when an electron-attracting phenyl substituent is present,[2] agrees with this interpretation.

The two kinetic terms on which the rate comparison is based are not only kinetically equivalent but must involve similar mechanistic pathways. The products of the reaction in the absence of bromide ion, when only the first term in eq 1 is applicable, reveal the presence of a cationic intermediate capable of reacting with the solvent. Under those conditions, phenylpropiolic acid affords a small amount of a mixture of *cis*- and *trans*-dibromocinnamic acids and extensive decarboxylation products, characteristic of a vinyl cation,[5] and ethyl phenylpropiolate affords *cis*- and *trans*-dibromo esters (13 and 23%) and solvent-incorporated products (64%) including ethyl bromobenzoylacetate. *trans*-Cinnamic acid and its ester yield in about equal amounts dibromides and bromohydrins (*erythro*-2-bromo-3-hydoxy-3-phenylpropanoic acid and ester) derived from *anti*- addition.[13] The exact nature of the intermediate ion cannot be specified with precision, but it is probably best represented as an open vinyl cation in the case of the acetylenic compound, and an unsymmetrical, weakly bridged carbonium ion in the case of the olefinic substrate.[14]

Details of the kinetics and product composition of these reactions will be discussed in forthcoming publications.

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(15) Taken in part from the Ph.D. Dissertation of S. DeYoung, Bryn Mawr College, May 1976, and the work for the Ph.D. Dissertation to be submitted by S. Ehrlich.

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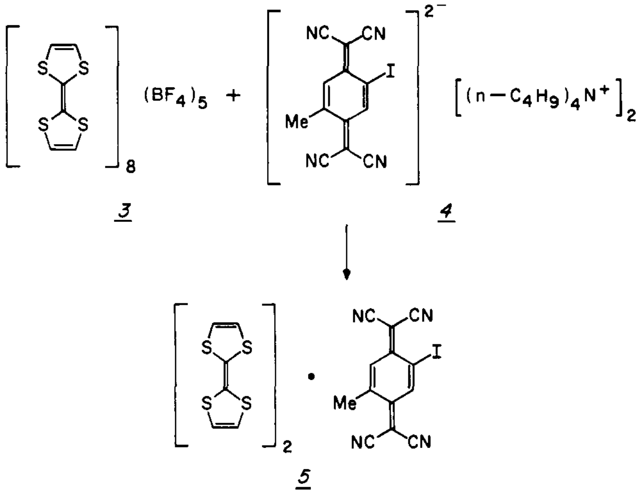
Variation of Stoichiometry in Tetrathiofulvalene–Tetracyanoquinodimethane Complexes

Sir:

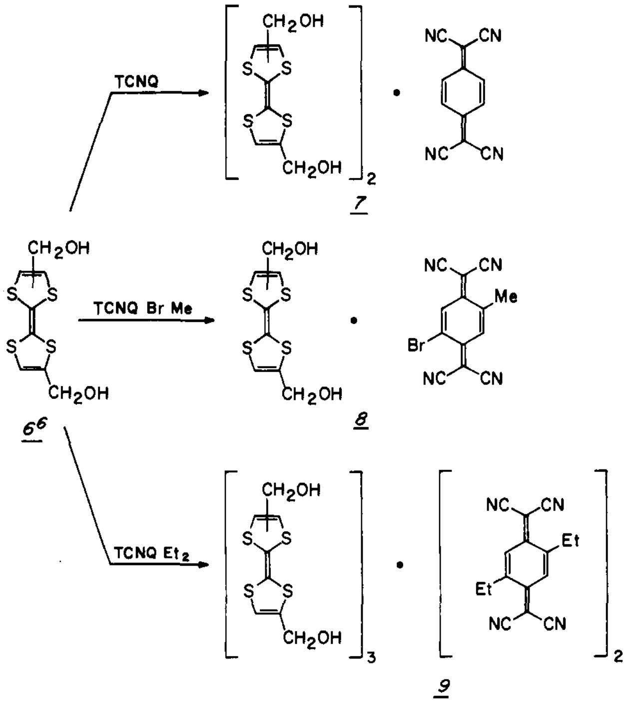
The 1:1 charge transfer complex between tetrathiofulvalene (TTF) and tetracyanoquinodimethane (TCNQ) has metallic electrical conductivity on the order of graphite.[1,2] The percent electron transfer in such complexes could have considerable influence on final electrical conductivity since electron transfer in turn may influence the ease of a Peierls transition to an insulating state, the ability to form closely packed homogeneous stacks of cations and anions, and electronic interactions in homogeneous cation and anion stacks once formed. One way to affect electron transfer is to vary electron acceptor or donor strengths; for example, in a series of 15 substituted TTF·TCNQ's, electrical conductivity increases by at least 10^4–10^7 on going from very strong electron acceptors such as $TCNQ(CN)_2$ or $TCNQF_4$ to weaker acceptors such as $TCNQEt_2$ or TCNQ.[3] A second way to affect electron transfer is to alter stoichiometry: for example, the electrically conductive band contributed by $TCNQ\cdot^-$ in **1** ($Et_3NH^+TCNQ\cdot^-$) is formally one-half full whereas the electrically conductive band contributed by $(TCNQ)_2\cdot^-$ in **2** ($Et_3NH^+(TCNQ)_2\cdot^-$) is formally one-fourth full. Again electrical conductivity is strongly affected since **2** is $\sim 10^9$ more conductive than **1**.[4]

The TTF·TCNQ system is one of the most conductive known. Attempts to increase this conductivity by changing stoichiometry from 1:1 have most often failed synthetically. For example, TTF·TCNQ itself has always been obtained as a 1:1 complex in spite of efforts to increase the proportion of TCNQ by crystallizing from a large excess of TCNQ.[1] Reaction of TTF with 16 substituted TCNQ's in acetonitrile has given 15 1:1 complexes and just one 2:3 complex.[5] We report here synthetic techniques and substitution patterns that easily make a wide range of stoichiometries available as quite highly conductive complexes in the TTF·TCNQ family.

A low temperature metathesis technique allows preparation of new stoichiometries between the same donor and acceptor. TTF and $TCNQICH_3$ precipitate from acetonitrile as a highly conductive 1:1 complex.[5] However, slurrying 0.85 g of ammonium salt **3** and 0.52 g of fluoroborate salt **4** under nitrogen for 2 h at −35 to −40 °C in 50 ml of acetonitrile and filtering cold affords 0.21 g (27%) of the blue-black 2:1 salt **5**. Infrared spectroscopy shows the absence of free TTF in **5**, since compound **5** totally lacks the strong TTF bands at 12.6 and 12.85 μ shown by a 1:1 mixture of TTF and $TTF\cdot TCNQICH_3$.



Mixing bis(hydroxymethyl)TTF **6** in refluxing acetonitrile with equimolar quantities of substituted TCNQ's and cooling precipitates complexes with 1:1, 3:2, and 2:1 stoichiometries.



Supporting data including compaction resistivities are shown in Table I.