Bull. Chem. Soc. Jpn., **56**, *2090—2092 (1983)* [Vol. 56, No. 7

IR Spectra of Solid State Reaction Products of TTF and Iodine

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(Received October 12, 1982)

IR spectra of the mixture of tetrathiafulvalene (TTF) and iodine showed that the two components react with each other in the solid state. Spectral changes with an increase in iodine content were analyzed on the basis of the spectra of TTF and the cations, and it was found that TTF is oxidized by iodine up to the dication in the solid state in contrast to the reaction in solution.

Tetrathiafulvalene (TTF) is known to form good electric conductors with various organic acceptors, *e.g.*, tetracyano-*p*-quinodimethan (TCNQ). The high electrical conductivity of the organic charge transfer salts such as TTF–TCNQ arises from the segregated stack crystal structure and the mixed-valence ground electronic state.[1] Such charge transfer salts have two stacks of donors and acceptors, both of which can potentially conduct, so that considerable complexities are encountered in the analysis of the solid state properties. On the other hand, TTF forms good conductors also with some inorganic anions, *e.g.*, halogens, which have only donor stacks. The single stack compounds should in principle provide simpler model systems for study on the electrical conductivity.

Recently Scott *et al.*[2] studied the crystal chemistry and phase compositions of TTF–halide systems to determine the compositional phase diagrams and to relate them to the important questions of structure and stability of these compounds. They obtained the salts by the reaction in solution. However, all the possible phases of the system are not always obtained as solid precipitates by the method because of the solubilities and the equilibria between the species. Other preparation methods should, therefore, be tried to obtain the whole phase diagram. We found the solid state reaction of TTF–iodine system. In this report, the IR spectra of the reaction products are measured and some information on the compositional phase diagram is obtained from the analysis of the spectra.

Experimental

TTF was synthesized by the method of Wudl *et al.*,[3] and recrystallized twice from hexane-cyclohexane and sublimed *in vacuo*. Iodine was obtained commercially and sublimed *in vacuo* from potassium iodide. Solid state reaction products were obtained by mixing of TTF and iodine in an agate mortar for several minutes at room temperature. A ratio of iodine atoms to TTF molecules is represented by the symbol "n". Composition of the mixtures ranged from n=0.2 to 40. A mixed-valence salt, $TTF\cdot I_{0.7}$, was prepared by the mixing of the stoichiometric amounts of the components in acetonitrile, and recrystallized from the solvent. A cation salt, $TTF\cdot I_3$, was prepared by the dropwise addition of the acetonitrile solution of TTF into the solution of excess iodine, and recrystallized from the solvent. A dication salt, $TTF\cdot Br_x$, was also obtained by the similar dropwise method in acetonitrile, but the recrystallization was not feasible because of the poor solubility. Elemental analyses showed that x=*ca.* 6; therefore, this salt is probably formulated as TTF^{2+} $(Br_3^-)_2$. All the sample prepared were dispersed in KBr, and the IR spectra were recorded on a JASCO DS-403G spectrometer.

Results and Discussion

IR spectra of TTF, $TTF\cdot I_{0.7}$, and $TTF\cdot I_3$ are shown in Fig. 1. The spectra of TTF and $TTF\cdot I_{0.7}$ agreed with those in the literature.[4,5] The spectrum of $TTF\cdot I_3$ also agreed with that of $TTF\cdot Br_{1.0}$ reported by Bozio *et al.*[4] except the small frequency shifts which are probably due to the difference in the counter ions. IR spectrum of $TTF(Br_3)_2$ is shown in Fig. 3a, which is similar to that of $TTF(BF_4)_2$ reported by Siedle *et al.*[6] except additional bands of BF_4^- in the latter. These results support the identification of the salts.

Of the features in these spectra, two absorption bands near 1500 and 1350 cm^{-1} are most suitable indications of the valence of TTF. The former, assigned to b_{1u} ν_{18} of TTF,[4] shows a large frequency shift with the change of the valence. The frequencies are: TTF, 1528 cm^{-1}; $TTF\cdot I_{0.7}$, 1500 cm^{-1}; $TTF\cdot I_3$, 1474 cm^{-1}; $TTF(Br_3)_2$, 1422 cm^{-1}. The other characteristic band near 1350 cm^{-1} is assigned to the out-of-phase combination mode of TTF a_g ν_3.[4] The vibronic interaction between the unpaired electron and the molecular vibration of TTF is responsible for the IR activity of this band;[4] therefore, the band appears only in the spectra of $TTF\cdot I_{0.7}$ and $TTF\cdot I_3$. The band of the former is much broader than that of the latter, and the two species, $TTF\cdot I_{0.7}$ and $TTF\cdot I_3$, are easily distinguished from the difference in the width. We analyze the IR spectrum of the solid state

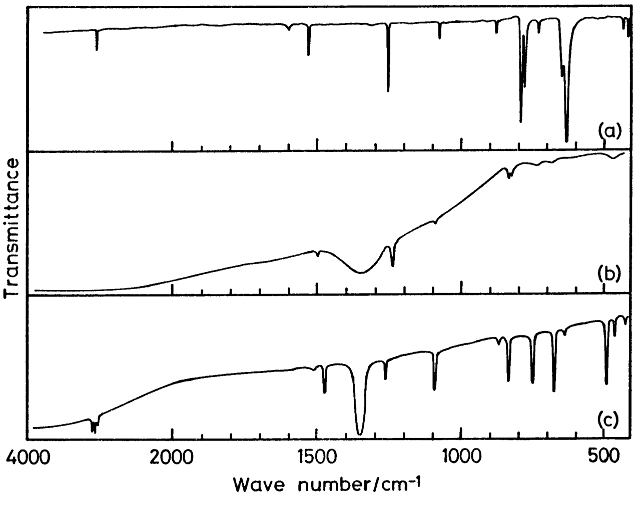

Fig. 1. IR spectra of (a) TTF, (b) $TTF\cdot I_{0.7}$, and (c) $TTF\cdot I_3$.

reaction products on the basis of the results for these TTF salts.

Spectral changes of TTF–iodine system with an increase in *n* are shown in Fig. 2. The changes may be interpreted as the stepwise oxidation of TTF, *i.e.*, $TTF \rightarrow TTF^{0.7+} \rightarrow TTF^{+} \rightarrow TTF^{2+}$, although a controversial feature is observed in the range, $n<0.7$: this will be discussed later. Absorption bands of TTF are decreasing with an increase in *n*. At $n=1$, features of $TTF^{0.7+}$ dominate the spectra and those of $TTF \cdot I_3$ also appear. The features of $TTF \cdot I_3$ grow up with *n*, and absorption bands of a new species appear at $n=4$. When *n* increases further, the new species comes to dominate the spectra, and only absorption bands of this species are observed at $n=20$. No further spectral changes occurred when *n* was increased up to 40; therefore, this species is probably the end product of this solid state reaction. The spectrum at $n=20$ is practically the same as that of $TTF(Br_3)_2$ as shown in Fig. 3. The result shows that iodine oxidizes TTF up to the dication in the solid state reaction. The sample of $n=20$ gave practically the same IR spectrum in Nujol mull as in the KBr disk. The former is black because of excess iodine whereas the latter is brown which may be attributed to the presence of I_2Br^- ion.

In the solution reaction, no dication salts have been obtained for TTF–iodine system. We also attempted to react TTF with a large excess of iodine to prepare the dication salt, but $TTF \cdot I_3$ was only obtained. Chlorine and bromine, on the other hand, easily oxidize TTF to the dication in solution.[2] The difference among the halogens is probably attributable to the weaker oxidizing ability of iodine than the others. Formation constant of the dication is expected to be rather small in the equilibrium, $TTF^{+}+nI_2 \rightleftharpoons TTF^{2+}(I_x^-)_2$. In the solid state, the environment of TTF remains iodine-rich during the whole oxidation processes and the dication species is formed. In solution, on the other hand, no dication salts will be obtained because TTF probably escapes from the iodine-rich environment, *i.e.*, the solution, as a precipitate of $TTF \cdot I_3$ before the further oxidation occurs.

No IR features of species other than TTF^{+} and TTF^{2+} are observed in the spectrum of $n>4$. The result shows that no homogeneous mixed-valence salt exists between the cation and the dication in contrast to the case between the neutral molecule and the cation, where $TTF^{0.7+}$ exists. Siedle *et al.*[6] reported a mixed-valence salt formulated as $(TTF^{+})(TTF^{2+})_2(CuCl_2^-)_5$, but the vibrational spectra are reasonably explained as a superposition of those of TTF^{+} and TTF^{2+}. Therefore, no valence fluctuation[7] occurs in this salt, in the time scale of molecular vibrations. The result shows striking difference in comparison with the case of homogeneous mixed-valence compounds such as $TTF \cdot I_{0.7}$, where two valence states, TTF and TTF^{+}, are indistinguishable from the vibrational spectra because the features of the two species are averaged out by the valence fluctuation.[8] The salt of Siedle *et al.* should, therefore, be considered inhomogeneous from the viewpoint of the vibrational characteristic time. The result in the present work does not rule out the possibility that such an inhomogeneous mixed-valence salt exists in TTF–iodine system.

In the range, $0<n<0.7$, an anomaly is observed

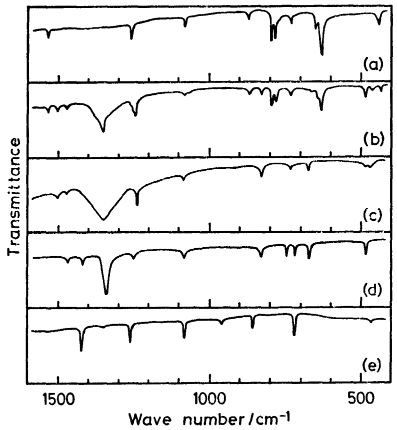

Fig. 2. IR spectra of solid state reaction products of TTF and iodine. (a) $n=0$; (b) 0.4; (c) 1; (d) 4; (e) 20.

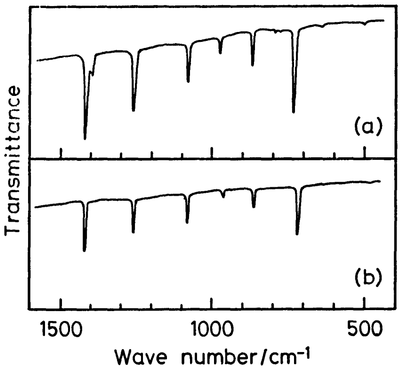

Fig. 3. IR spectra of (a) $TTF(Br_3)_2$ and (b) sample of $n=20$.

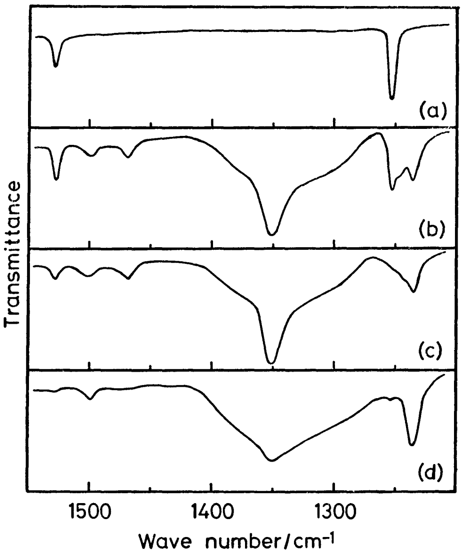

Fig. 4. IR spectra of solid state reaction products of TTF and iodine. (a) $n=0$; (b) 0.3; (c) 0.4; (d) 0.7.

in the spectra, as mentioned above. In order to show the detailed feature of the spectra, the region of 1200—1600 cm^{-1} is given in an expanded scale (Fig. 4). IR spectra of the samples were obtained also in Nujol and hexachlorobutadiene mull, and the spectra agreed well with those in the KBr disk. The samples of $n=0.3$ and 0.4 clearly exhibit three absorption bands at 1528, 1500, and 1470 cm^{-1}, which are attributable to the b_{1u} ν_{18} modes of TTF, TTF$^{0.7+}$, and TTF^{+}, respectively. Another triplet structure is observed also in the region of b_{2u} ν_{23}, 1230—1250 cm^{-1}.$^{4)}$ Furthermore, the characterictic broad band near 1350 cm^{-1} has an anomalous profile, which is probably due to the superposition of sharp and broad features of TTF^{+} and TTF$^{0.7+}$. These results clearly show that the reaction product contains not only TTF$^{0.7+}$ but also TTF^{+} even under the condition of a fairly small iodine content. The equilibrium is expected to shift to TTF^{+}, if n is increased. However, the result was obtained contrary to this expectation as shown in Fig. 4; *i.e.*, TTF$^{0.7+}$ came to dominate the spectrum with an increase in n. The TTF^{+} species above is not probably the triiodide salt because the iodine content is fairly small and the frequency of the vibronically allowed band, 1355 cm^{-1}, is distinct from that of TTF$\cdot$I$_3$, 1345 cm^{-1}. Only the candidate will be TTF$\cdot$I$_{1.0}$, which has not been obtained by the reaction in solution.

The cause of this anomaly may be attributable to a cluster structure of the cation in TTF–iodine mixture. The ionization potential of TTF is small and the electron affinities of halogens are large, so that TTF is present only as the fully ionic form, TTF^{+} and (TTF^{+})$_2$,$^{9)}$ in the solution of TTF–halides. In the crystals of nonstoichiometric TTF–halides, on the other hand, the mixed-valent state is stabilized by the balance of the energy cost with the ionization of the donor–acceptor pairs and the energy gain by the electrostatic interaction (crystal Madelung energy);$^{10)}$ in other words, mixed-valent states are stable only in the crystal. These facts suggest that TTF molecules have the fully ionic and the mixed-valent states in the small and large clusters respectively, *i.e.*, the state changes at a boundary size of the cluster. The fraction of the large clusters increases with an increase in n, and this will result in the spectral change observed. Such a fully ionic-to-mixed-valent transition of TTF state is interesting from the viewpoint of the stability of mixed-valent TTF salts. Some information will be obtained from, *e.g.*, vibrational spectra of the aggregates of TTF^{+} in an inert gas matrix at low temperature.

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