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Space Effects of Tetra-*n*-alkyl Ammonium Ions on the Electrical Conduction of Tetracyanoquinodimethane Salts

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Several papers have been reported on the electrical properties of several kinds of TCNQ complexes,[1,2] but little attention has been paid to the effects of the molecular structure of paired ion on their electrical conduction.[3]

In this work we investigated how the electrical conductivities of TCNQ salts and complexes depend on the size of ammonium ions. Seven sorts of simple salts and six sorts of complex salts of TCNQ were prepared with various tetra-*n*-alkyl ammonium ions as the paired cation, and the space effects of these ammonium ions on the electrical conductivity were investigated. It was found that the electrical conductivities decrease with an increase in the number of carbon atoms in *n*-alkyl groups for the simple salts: on the other hand, for the complex salts the minimum resistivity appears when the tetra-*n*-butyl ammonium ion is used.

Experimental

Formation of Simple Salts. Tetra-*n*-alkyl ammonium halides and equimolar K^+ $TCNQ^-$ were dissolved and mixed in acetonitrile or ethyl acetate. After the potassium halide and solvent had been removed, the crude salt crystals were collected. These crystals were washed with water and dried, and were purified by means of recrystallization from the solvent used in the preparation.

Simple salts of tetra-*n*-amyl and tetra-*n*-hexyl ammonium were pasty and could not be dried completely even under reduced pressure for a long time.

The analytical results and preparation conditions of simple salts are summarized in Table 1.

Preparation of Complex Salts. TCNQ simple salt and equimolar neutral TCNQ were crushed into powder, mixed completely in an agate bowl, and dissolved in dried acetonitrile. After this had been kept at 70°C for one hour, blue-black plate crystals of complex salt were precipitated. Their elementary analytical data are listed in Table 2.

Measuring of Electrical Conductivity. The electrical conductivities of these specimens were measured by a method reported previously.[4]

Results and Discussion

TCNQ Simple Salts. Their electrical resis-

TABLE 1. TCNQ SIMPLE SALTS CONTAINING TETRA-*n*-ALKYL AMMONIUM CATION

Product	Cation source	Solvent used for preparation	Condition of preparation		Elementary analysis			
$NH_4\cdot TCNQ$	NH_4Cl	*			Calcd Found	64.9 63.9	3.6 3.7	31.5 31.1
$(CH_3)_4N\cdot TCNQ$	$(CH_3)_4N\cdot Br$	CH_3CN	80°C	2 hr	Calcd Found	69.1 68.2	5.8 5.6	25.2 24.5
$(C_2H_5)_4N\cdot TCNQ$	$(C_2H_5)_4N\cdot Br$	CH_3CN	70°C	2 hr	Calcd Found	71.9 71.6	7.2 7.4	21.0 20.7
$(C_3H_7)_4N\cdot TCNQ$	$(C_3H_7)_4N\cdot I$	$CH_3COOC_2H_5$	r.t.	2 hr	Calcd Found	73.8 74.2	8.2 8.3	17.9 16.9
$(C_4H_9)_4N\cdot TCNQ$	$(C_4H_9)_4N\cdot I$	$CH_3COOC_2H_5$	r.t.	2 hr	Calcd Found	75.8 75.3	9.1 8.9	15.7 14.9
$(C_5H_{11})_4N\cdot TCNQ$	$(C_5H_{11})_4N\cdot Br$	CH_3CN	70°C	2 hr	Calcd Found	76.5 77.0	9.6 10.0	13.9 13.7
$(C_6H_{13})_4N\cdot TCNQ$	$(C_6H_{13})_4N\cdot I$	$CH_3COOC_2H_5$	r.t.	4 hr	Calcd Found	77.4 77.4	10.0 10.5	12.5 11.9

* Equimolar NH_4Cl and KTCNQ were ground into powder by an agate bowl and extracted with $CH_3COOC_2H_5$.

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1) W. J. Siemons, P. E. Bierstedt and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).
2) H. Scott, P. L. Knonick, R. Chairge and M. M. Labes, *J. Phys. Chem.*, **69**, 1740 (1965).
3) P. Dupuis and J. Neel, *C. A. Acad, Sci. Paris, Ser C.*, **265**, 688 (1967).
4) S. Nishizaki and H. Kusakawa, This Bulletin, **36**, 1681 (1963).

TABLE 2. TCNQ COMPLEX SALTS CONTAINING TETRA-*n*-ALKYL AMMONIUM CATION

Product	Elementary analysis Calcd C	H	N	Found C	H	N
$(CH_3)_4N\cdot(TCNQ)_2$	69.7	4.1	26.1	70.2	4.3	25.5
$(C_2H_5)_4N\cdot(TCNQ)_2$	71.3	5.2	23.4	71.1	5.3	23.3
$(C_3H_7)_4N\cdot(TCNQ)_2$	72.7	6.1	21.2	72.6	6.1	21.1
$(C_4H_9)_4N\cdot(TCNQ)_2$	73.8	6.8	19.4	74.0	6.6	19.5
$(C_5H_{11})_4N\cdot(TCNQ)_2$	74.8	7.4	17.9	74.9	7.2	17.5
$(C_6H_{13})_4N\cdot(TCNQ)_2$	75.6	7.9	16.5	75.5	8.1	16.2

tivities at room temperature and the temperature dependence (activation energy) of the resistivity are summarized in Table 3. As Table 3 shows, tetra-*n*-alkyl ammonium-TCNQ simple salts can be classified into three groups; ammonium, tetramethyl- and tetraethylammonium salts belong to

TABLE 3. ELECTRICAL RESISTIVITY AND ACTIVATION ENERGY OF TCNQ SIMPLE SALTS

Simple salt	Resistivity at 20°C (Ωcm)	Activation energy *E* (eV)
$NH_4\cdot TCNQ$	4.3×10^4	0.22
$(CH_3)_4N\cdot TCNQ$	3.4×10^5	0.22
$(C_2H_5)_4N\cdot TCNQ$	$1.0+10^6$	0.28
$(C_3H_7)_4N\cdot TCNQ$	1.6×10^9	0.87
$(C_4H_9)_4N\cdot TCNQ$	4.8×10^{10}	0.88
$(C_5H_{11})_4N\cdot TCNQ$	non reproducible	
$(C_6H_{13})_4N\cdot TCNQ$	non reproducible	

the first, tetra-*n*-propyl- and tetra-*n*-butylammonium salts to the second, and tetra-*n*-amyl- and tetra-*n*-hexylammonium salts to the last group. The activation energies of salts in the first group are approximately 0.22 eV, and their resistivities become higher as the constructing-cation size increases. Of the second group of salts both the resistivity and the activation energy are much larger in magnitude in the first. The resistivities of the third group of salts could not be obtained with a good reproducibility. For tetra-*n*-alkylammonium-TCNQ simple salts a lower resistivity appears on the salt with a smaller ammonium ion size.

TCNQ Complex Salts. The resistivity and activation energies for the complex salts are listed in Table 4. In Fig. 1 the magnitudes of both the resistivity at 20°C and the activation energy of resistivity are plotted *vs.* the number of carbon atoms in the alkyl group.

For complex salts both the resistivity and the activation energy gradually decrease in magnitude with an increase in the ammonium ion size, the minimum values appearing at tetra-*n*-butylammonium complex salt. After this minimum points, each value rapidly increases again.

TABLE 4. ELECTRICAL RESISTIVITY AND ACTIVATION ENERGY OF COMPLEX SALTS

Complex salt	Resistivity at 20°C (Ωcm)	Activation energy *E* (eV)
$(CH_3)_4N\cdot(TCNQ)_2$	1.1×10^6	0.37
$(C_2H_5)_4N\cdot(TCNQ)_2$	3.3×10^4	0.34
$(C_3H_7)_4N\cdot(TCNQ)_2$	9.9×10^3	0.33
$(C_4H_9)_4N\cdot(TCNQ)_2$	9.7×10^1	0.21
$(C_5H_{11})_4N\cdot(TCNQ)_2$	1.0×10^7	0.75
$(C_6H_{13})_4N\cdot(TCNQ)_2$	4.6×10^8	0.93

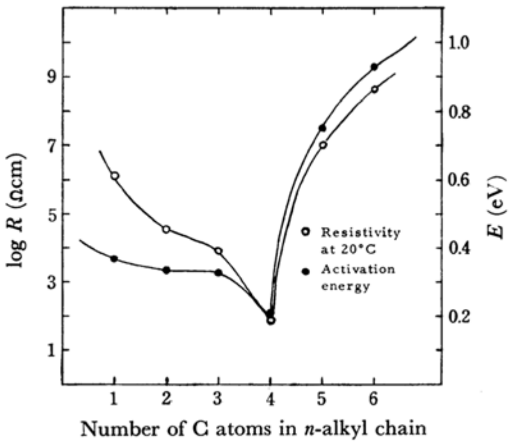

Fig. 1. Relation between resistivity and activation energy and carbon number of *n*-alkyl group in ammoniumion contained in TCNQ complex salts.

The crystal formation and electrical conductivity of complex salts are affected by the size of the paired ammonium ions. The crystal of ammonium complex salt could not be obtained, and the preparation of tetramethyl- and tetra-*n*-hexylammonium complex salts was difficult. It seems that the ammonium ion size influences the arrangement of TCNQ molecules in the complex crystal and that the overlapping of the molecular orbitals on TCNQ is varied. When the paired cation in the complex crystal is the tetra-*n*-butylammonium ion, the arrangemetn of the TCNQ molecule reaches the optimum for electrical conduction. As the ion size of the paired cation is either smaller or larger than with tetra-*n*-butylammonium, the overlapping of moleculals on TCNQ decreases, thus leading to lower electrical conductivity.