NOTES *Bull. Chem. Soc. Jpn.*, **54**, 617—618 (1981)

Effect of Halogen Substituents of Anion Radicals on the Electronic States of Crystalline Anion Radical Salts; K^+ *p*-Chloranil$^{\cdot-}$, K^+ 2,5-Dibromo-3,6-dichloro-*p*-benzoquinone$^{\cdot-}$, and K^+ *p*-Bromanil$^{\cdot-}$

Yôichi Iida

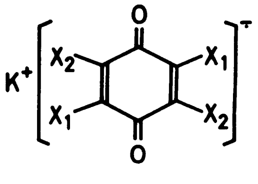
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received July 23, 1980)

Synopsis. The intermolecular interactions in crystalline anion radical salts of K^+ *p*-Chloranil$^{\cdot-}$, K^+ 2,5-Dibromo-3,6-dichloro-*p*-benzoquinone$^{\cdot-}$, and K^+ *p*-Bromanil$^{\cdot-}$ were examined in terms of one-dimensional half-occupied Hubbard model. Effect of substituents of the anion radicals on the crystal electronic states was discussed with the parameter values estimated by the Hubbard model.

Many papers have been written on the prominent magnetic, electrical and optical properties of a number of crystalline ion radical salts.[1-4] In such ion radical salts, the planar ion radical molecules are known to form, in themselves, a segregated stacking into one-dimensional columns so as to make a large overlap between their half-occupied molecular orbitals. In this case, since any individual radical molecule interacts through charge transfer most strongly with two adjacent radicals, the electronic and magnetic properties of the solid salt differ distinctly from those of the ion radical monomer.[1] In a previous paper,[3] we examined crystalline anion radical salts derived from halogen-substituted *p*-benzoquinones, and explained their optical and magnetic properties by applying half-occupied Hubbard model to the segregated stacks of those *p*-benzoquinone anion radicals. In the present paper, we take K^+ *p*-Chloranil$^{\cdot-}$, K^+ 2,5-Dibromo-3,6-dichloro-*p*-benzoquinone$^{\cdot-}$, and K^+ *p*-Bromanil$^{\cdot-}$, and compare the magnitudes of the Hubard-model parameters together with the ground-state stabilization energies of those anion radical salts.[5] Since the counter K^+ cation is common, we shall discuss the effect of halogen substituents of the anion radicals on the electronic states of those anion radical salts.

First, we consider the electronic state of solid K^+ *p*-Chloranil$^{\cdot-}$ salt. At room temperature, although there are several polymorphs, in the structure of the orthorhombic α-form, the *p*-chloranil anion radicals are stacked in themselves with equal intervals, forming non-alternant one-dimensional columns parallel to the c-axis, the interplanar spacing being 3.47 Å.[6] The K^+ ion lies at a center of a rectangle formed by four oxygen atoms of the *p*-chloranil anion radicals related by the c translation. In order to understand the optical and magnetic properties of this salt, we applied non-alternant one-dimensional half-occupied Hubbard model to the segregated stack of the *p*-chloranil anion radicals.[3] This model is a simplification of the real crystal and is described by two parameters, I and T.[7] Here, T is the transfer matrix element of an unpaired electron which describes hopping between adjacent molecular sites, while I is the Coulomb repulsion between two electrons with up and down spins on the same site. Then, T favors electron delocalization through band formation, whereas I favors localization due to electron-electron repulsions. On the basis of this model, we can well understand the reasons why the intermolecular charge-transfer absorption appears in the solid-state spectrum of K^+ *p*-Chloranil$^{\cdot-}$ at 11800 cm^{-1} and why the antiferromagnetic spin exchange interaction, $J=113$ cm^{-1}, acts between adjacent *p*-chloranil anion radicals.[2-4] The values of $I=11800$ cm^{-1} and $T=-820$ cm^{-1} explain well those observed optical and magnetic data of K^+ *p*-Chloranil$^{\cdot-}$. Once the I and T values are obtained experimentally, it is easy to determine the magnitude of ground-state energy stabilization, E, due to charge-transfer interaction between ion radicals in non-alternant one-dimensional system of the ion radicals. In previous papers,[4] we obtained in a limit of $I/|T|=\infty$ the expression of $E=-(4NT^2/I)\ln 2$, where N is the number of ion radicals. In the case of the one-dimensional system of *p*-chloranil anion radicals, where $I=11800$ cm^{-1} and $T=-820$ cm^{-1}, the magnitude of $I/|T|=14.39\cdots$ is found to be much larger than unity. Therefore, the condition of $I/|T|=\infty$ is approximately fulfilled in our case, and the value of E is estimated to be -1.87 kJ mol^{-1}.



(a); $X_1=X_2=Cl$
(b); $X_1=X_2=Br$
(c); $X_1=Br$, $X_2=Cl$

Fig. 1. Halogen-substituted *p*-benzoquinone anion radical salts with potassium cation; (a) *p*-chloranil anion radical salt, (b) *p*-bromanil anion radical salt, and (c) 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (*p*-QBr_2Cl_2) anion radical salt.

In a similar way, the electronic state of solid K^+ *p*-Bromanil$^{\cdot-}$ salt was analyzed in terms of a segregated stack of *p*-bromanil anion radicals. The non-alternant one-dimensional half-occupied Hubbard model was then applied to this segregated stack, and the values of $I=10900$ cm^{-1} and $T=-730$ cm^{-1} were obtained.[3] Since the magnitude of $I/|T|=14.93\cdots$ is also much larger than unity, the ground-state stabilization energy, E, in the one-dimensional system of *p*-bromanil anion radicals is calculated, in a way similar to the case of *p*-chloranil anion radicals, to be -1.61 kJ mol^{-1}.

As for the electronic state of solid K^+ *p*-$QBr_2Cl_2^{\cdot-}$ salt, two models were previously proposed to explain its optical and magnetic properties; one is a dimer model of p-QBr$_2$Cl$_2$ anion radicals and the other, non-alternant one-dimensional model of p-QBr$_2$Cl$_2$ anion radicals.[3] However, because of the reason given in Ref. 8, the latter model is more probable in K$^+$ p-QBr$_2$Cl$_2^{\cdot}$ than the former model, and our approach of non-alternant one-dimensional half-occupied Hubbard model is still applicable to that system. The values of $I=11500\ \text{cm}^{-1}$ and $T=-750\ \text{cm}^{-1}$ were thus estimated for the one-dimensional system of p-QBr$_2$Cl$_2$ anion radicals. When we note that $I/|T|=15.33\cdots$ is also much greater than unity, the ground-state stabilization energy, E, of this system is calculated to be -1.61 kJ mol^{-1} by using the estimated I and T values.

In the following, we compare the magnitudes of the parameters in the Hubbard model, that is, on-site Coulomb repulsion (I), transfer matrix element (T) and ground-state stabilization energy (E) estimated for K$^+$ p-Chloranil$^{\cdot}$, K$^+$ p-QBr$_2$Cl$_2^{\cdot}$, and K$^+$ p-Bromanil$^{\cdot}$ salts. Since the counter K$^+$ cation is common to these salts, and since all the anion radicals are closely related chloro- and bromo-substituted p-benzoquinone anion radicals, the difference in the values of those physical parameters should come from the difference in the substituents of the anion radicals. As for the on-site Coulomb repulsion, I, the order of its magnitude is found to be $11800\ \text{cm}^{-1}$ (p-Chloranil$^{\cdot}$)$>11500\ \text{cm}^{-1}$ (p-QBr$_2$Cl$_2^{\cdot}$)$>10900\ \text{cm}^{-1}$ (p-Bromanil$^{\cdot}$). The magnitude of Coulomb repulsion between two electrons with up and down spins on the same site will be decreased if the molecular size of ion radical is extended and if polarizable substituents are introduced into ion radical. In this respect, we can understand the successive decrease of on-site Coulomb repulsion in going from p-chloranil anion radical to p-QBr$_2$Cl$_2$ and p-bromanil anion radicals, because the replacement of chloro-substituents of the anion radical by bromo-substituents leads to the expansion of the size of the molecule and also to the introduction of more polarizable substituents into the anion radical.

The transfer matrix element, T, between adjacent anion radical molecules is closely related to the overlap integral between the half-occupied molecular orbitals of the anion radicals. The absolute values of $|T|$ are found to range as $820\ \text{cm}^{-1}$ (p-Chloranil$^{\cdot}$)$>750\ \text{cm}^{-1}$ (p-QBr$_2$Cl$_2^{\cdot}$)$>730\ \text{cm}^{-1}$ (p-Bromanil$^{\cdot}$). This result is also reasonable, because the replacement of the chloro-substituents in the anion radical by the bulky bromo-substituents increases the intermolecular spacing between adjacent anion radicals, and thus, decreases definitely the overlap between their half-occupied molecular orbitals.

As for the ground-state stabilization energy due to charge-transfer interaction between anion radicals, E, the absolute value of 1.87 kJ mol^{-1} of p-chloranil anion radical salt is greatest. The value of 1.61 kJ mol^{-1} of p-QBr$_2$Cl$_2$ anion radical salt coincides with that of 1.61 kJ mol^{-1} of p-bromanil anion radical salt, and these two values are smaller than the 1.87 kJ mol^{-1} value of p-chloranil anion radical salt. As has been mentioned, the ground-state stabilization energy, E, is given by $-(4NT^2/I)\ \ln 2$, and both I and $|T|$ values decrease progressively in going from p-chloranil anion radical salt to p-QBr$_2$Cl$_2$ and p-bromanil anion radical salts. However, the value of T^2/I is found to be greatest in p-chloranil anion radical salt. For p-QBr$_2$Cl$_2$ and p-bromanil anion radical salts, although both I and $|T|$ values of the former salt are larger than those of the latter salt, the quantities of T^2/I are of the same magnitudes.

References

1) See, for example, Z. G. Soos and D. J. Klein, "Molecular Association," ed by R. Foster, Academic Press, London, New York, San Francisco (1975), Vol. 1, Chap. 1, and the references cited therein.

2) Y. Iida, *Bull. Chem. Soc. Jpn.*, **50**, 1445, 2481 (1977); **51**, 434, 631, 1549, 3637 (1978); **52**, 689, 1523, 2791 (1979).

3) Y. Iida, *Bull. Chem. Soc. Jpn.*, **51**, 2523 (1978).

4) Y. Iida, *Bull. Chem. Soc. Jpn.*, **52**, 3447 (1979); **53**, 1447 (1980).

5) Hereafter, 2,5-dibromo-3,6-dichloro-p-benzoquinone is *abbreviated as p-QBr$_2$Cl$_2$, and its anion radical salt with* potassium cation, as K$^+$ p-QBr$_2$Cl$_2^{\cdot}$.

6) M. Konno, H. Kobayashi, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 1987 (1973).

7) J. Hubbard, *Proc. R. Soc. London, Ser. A*, **276**, 238 (1963); **281**, 401 (1964).

8) According to Ref. 3, if dimer Hubbard model is applied to p-QBr$_2$Cl$_2$ anion radicals in solid K$^+$ p-QBr$_2$Cl$_2^{\cdot}$ salt, the values of I and T have been reported to be $11300\ \text{cm}^{-1}$ and $-710\ \text{cm}^{-1}$, respectively. Then, the ground-state stabilization energy due to charge-transfer interaction between p-QBr$_2$Cl$_2$ anion radicals in a dimer is given by $I/2-\sqrt{(I/2)^2+(2T)^2}=-153\ \text{cm}^{-1}$ per dimer or -0.92 kJ mol^{-1}. On the other hand, if non-alternant one-dimensional model is applied to the anion radicals, the ground-state stabilization energy is estimated to be -1.61 kJ mol^{-1} (see text). Unfortunately, at the present time, no data on the crystal Madelung energy, which is a major source of cohesive energy, are available for K$^+$ p-QBr$_2$Cl$_2^{\cdot}$ salt. However, if the Madelung energy of the crystal lattice of the dimer model is almost the same as that of the one-dimensional model, the ground-state stabilization energy due to the charge-transfer interaction becomes important for the cohesive energy. In this respect, the ground state of the non-alternant one-dimensional model seems to be more stable in K$^+$ p-QBr$_2$Cl$_2^{\cdot}$ salt than that of the dimer model.