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The Electronic Spectra of the Anion Radical Salts Derived from Halogen-substituted *p*-Benzoquinones*[1]

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The anion-radical salts derived from *p*-chloranil, 2,5-dibromo-3,6-dichloro-1,4-benzoquinone, and *p*-bromanil were prepared. The absorption spectra in an acetone solution and the diffuse reflection spectra of the solid salts were examined. These solid salts were then classified into three groups, namely, those showing the spectrum of the anion-radical monomer, those showing a strong charge-transfer band characteristic of the solid salts, and, finally, those showing not only the spectrum of the anion-radical monomer but also an intermolecular charge-transfer band. The mode of intermolecular interaction in these anion-radical salts was discussed according to this classification. Their magnetic behaviour was also speculated upon on the basis of the charge-transfer interaction.

Solid ion-radical salts are particularly interesting because, in crystals of such ion-radical salts, the ion-radical molecules form, in themselves, a plane-to-plane stacking into columns so as to make a large overlap between their half-filled molecular orbitals.[1] Since, in this case, any individual radical molecule interacts through charge transfer most strongly with one or two other radicals, the electronic spectrum of the solid salt is expected to be different from the monomer spectrum in solution and to show an intermolecular charge-transfer band. In this respect, it was interesting to examine the solid-state spectra, particularly of Würster cation-radical salts and of 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion-radical salts.[2-4]

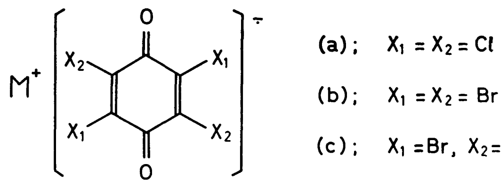

Fig. 1. The anion-radical salts of (a) *p*-chloranil, (b) *p*-bromanil, and (c) 2,5-dibromo-3,6-dichloro-1,4-benzoquinone. M^+ represents a diamagnetic counter cation.

The present paper will describe the solid-state spectra, as well as the absorption spectra in solution, of some stable anion-radical (*i.e.*, semiquinone ion) salts derived from halogen-substituted *p*-benzoquinones (see Fig. 1). The purpose of this paper is to report the results of our electronic-spectrum measurements and to show that a charge-transfer interaction similar to those in Würster cation-radical salts and in TCNQ anion-radical salts takes place in these anion-radical salts. It is also interesting to discuss their magnetic properties on the basis of the charge-transfer interaction.

Experimental

Materials. The *p*-chloranil and *p*-bromanil were commercially available. The 2,5-dibromo-3,6-dichloro-1,4-benzoquinone (*p*-QBr_2Cl_2) was synthesized by the bromination of 2,5-dichloro-1,4-benzoquinone. These compounds were purified by recrystallization from benzene or acetic acid.

The following six anion-radical salts were prepared according to the method of Torrey and Hunter[5]: Na^+ *p*-Chloranil$^{\overline{\cdot}}$, K^+ *p*-Chloranil$^{\overline{\cdot}}$, Na^+ *p*-$QBr_2Cl_2^{\overline{\cdot}}$, K^+ *p*-$QBr_2Cl_2^{\overline{\cdot}}$, Na^+ *p*-Bromanil$^{\overline{\cdot}}$, and K^+ *p*-Bromanil$^{\overline{\cdot}}$. In this method, the anion-radical salts were made by the one-electron reduction of the corresponding quinones with alkali metal iodides in a cold acetone solution.

Measurements. The absorption spectra in an acetone solution were measured at room temperature, using a Beckman DK-2A spectrophotometer at concentrations of the order of 10^{-4} mol/*l*.

The diffuse reflection spectra of the solid salts were

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[1] This work was presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969, and at the Symposium on Molecular Structure, Fukuoka, October, 1969.

1) G. R. Anderson and C. J. Fritchie, Jr., Second National Meeting, Society for Applied Spectroscopy, San Diego, October, 14, Paper 111 (1963); C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 892 (1966); C. J. Fritchie, Jr., and P. Arthur, Jr., *ibid.*, **21**, 139 (1966); P. Goldstein, K. Seff and K. N. Trueblood, *ibid.*, **B24**, 778 (1968); J. Tanaka and N. Sakabe, *ibid.*, **B24**, 1345 (1968).

2) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

3) Y. Iida, *ibid.*, **42**, 71 (1969).

4) Y. Iida, *ibid.*, **42**, 637 (1969).

5) H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).

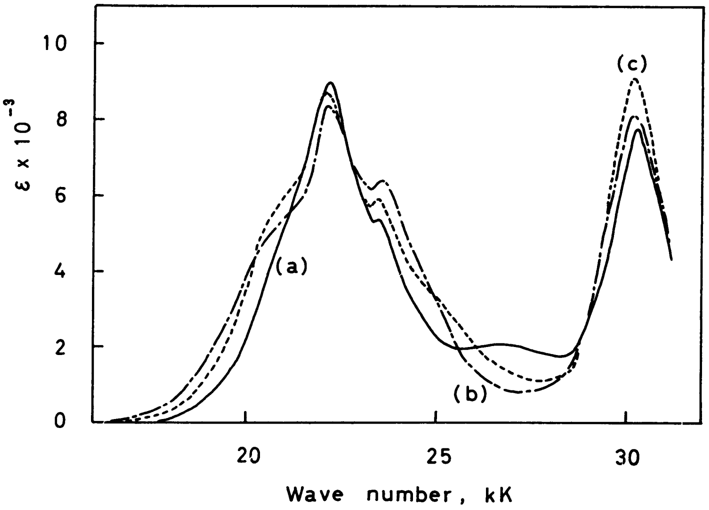

Fig. 2. The absorption spectra of (a) K^+ p-Chloranil$^{\overline{\cdot}}$, (b) K^+ p-Bromanil$^{\overline{\cdot}}$ and (c) K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$, in acetone solution.

recorded on a Beckman DK-2A spectroreflectometer in the range from 4.0 to 30.8 kK at room temperature. In order to avoid cation exchange between the salt and the diluent, the sodium salts were ground with sodium chloride, and the potassium salts, with potassium bromide. The solid-state spectra were then obtained by plotting the diffuse reflection spectra using the Kubelka-Munk equation, $f(R)=(1-R)^2/2R$, in which R is the reflectance. The experimental details were the same as those in previous papers.[2-4)]

The Absorption Spectra in Solution

Some of the absorption spectra of these anion-radical salts in an acetone solution are given in Fig. 2. The spectra are not changed when the counter cation of the salt is replaced. Since the concentrations are so dilute, the salts seem to be completely dissociated. The obtained spectra are those of the anion-radical monomer, because the counter cations of the salts are simple alkali metal cations.

The *p*-Chloranil Anion Radical (Fig. 2, Curve a). The absorption spectrum of this anion was found to be very similar to that of the *p*-benzoquinone anion-radical reported by Harada and Inokuchi.[6)] The spectrum of the *p*-chloranil anion-radical consists of bands at 22.2 kK, 26.7 kK, and 30.3 kK, while that of the *p*-benzoquinone anion-radical has bands at 22.7 kK, 27.0 kK, and 31.3 kK. We can see that the introduction of the chlorine substituents into the *p*-benzoquinone anion-radical causes slight shifts in their corresponding bands. Therefore, it may be assumed that the π-conjugated system for the *p*-chloranil anion-radical may be approximated by that for the *p*-benzoquinone anion-radical. According to Harada's calculations,[7)] the ground configuration of the *p*-benzoquinone anion-radical belongs to the $^2B_{3g}$ representation. He assigned the bands at 22.7 kK, 27.0 kK, and 31.3 kK to the transitions of $^2B_{3g}\rightarrow{}^2B_{1u}$, $^2B_{3g}\rightarrow{}^2A_u$, and $^2B_{3g}\rightarrow{}^2B_{1u}$ respectively. Therefore, the same assignments seem to be applicable to the bands at 22.2 kK, 26.7 kK, and 30.3 kK for the *p*-chloranil anion-radical.

On the other hand, Shirotani *et al.* have found the monomer-dimer equilibrium for the *p*-chloranil anion-radicals in an ethanolic solution at low temperatures.[8)] At this time, the charge-transfer band of the dimer[*2] appears around 14.9 kK; this value is smaller than that of 17.1 kK for the dimer of the *p*-benzoquinone anion-radical reported by Kimura *et al.*[9)]

The *p*-Bromanil Anion Radical (Fig. 2, Curve b). Because both were similar to those for the *p*-chloranil anion-radical, the bands at both 22.2 kK and 30.2 kK for the *p*-bromanil anion-

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6) Y. Harada and H. Inokuchi, *Mol. Phys.*, **8**, 265 (1964).

7) Y. Harada, *ibid.*, **8**, 273 (1964).

8) I. Shirotani, N. Sakai and S. Minomura, This Bulletin, to be published.

[*2] According to the Hausser and Murrell's theory, the ion-radicals in a dimer may lie in parallel planes, one above the other, and the spin-exchange interaction leads to a singlet ground state and an excited triplet state. Therefore, we must take into consideration the fact that intermolecular charge-transfer may make a significant contribution to stabilizing the ground singlet state of the dimer. The low-energy charge-transfer absorption characteristic of the dimer arises from a transition from the thus-stabilized ground state to an excited singlet state expressed by an antisymmetric combination of the wave-functions for charge-transfer structures, R-R^{2-}. See K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

9) K. Kimura, H. Yamada and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).

radical were assigned to the transitions of ${}^2B_{3g}\rightarrow{}^2B_{1u}$. However, it was noted that, unlike the *p*-chloranil anion-radical, the transition due to ${}^2B_{3g}\rightarrow{}^2A_u$ was not detected, while a shoulder appeared around 20.5 kK.

The *p*-QBr_2Cl_2 Anion Radical (Fig. 2, Curve c). The point group for this molecule belongs to the C_{2h} symmetry, which is degraded from the D_{2h} symmetry for the above two molecules. Therefore the bands at both 22.1 kK and 30.2 kK must belong to the ${}^2B_g\rightarrow{}^2A_u$ transitions. Except for this difference, the electronic structures of the *p*-QBr_2Cl_2 and *p*-bromanil anion-radicals seem to be much alike.

The Solid-State Spectra

K$^+$ *p*-Chloranil$^{\overline{\cdot}}$ (Fig. 3, Curve a). The solid-state spectrum of this salt shows a low-energy band at 11.8 kK, a strong high-energy band at 23.3 kK, and a shoulder around 30 kK. Except for the appearance of the low-energy band, the bands seem to be similar to those for the *p*-chloranil anion-radical monomer in an acetone solution. Therefore, the high-energy band at 23.3 kK and the shoulder around 30 kK can be assigned to the ${}^2B_{3g}\rightarrow{}^2B_{1u}$ transitions at 22.2 kK and at 30.3 kK respectively for the monomer. Unfortunately, in the present investigation, the band due to the ${}^2B_{3g}\rightarrow{}^2A_u$ transition for the monomer spectrum was not observed for the solid-state spectrum. Although the value of the low-energy band, 11.8 kK, of the solid-state spectrum is a little bit lower than that of 14.9 kK of the charge-transfer band of the *p*-chloranil anion-radical dimer in solution, we assigned this band to the charge-transfer transition in the solid state. However, the intensity of this band is rather weaker than that of Na$^+$ *p*-Chloranil$^{\overline{\cdot}}$ (see below).

Na$^+$ *p*-Chloranil$^{\overline{\cdot}}$ (Fig. 3, Curve b). Unlike K$^+$ *p*-Chloranil$^{\overline{\cdot}}$, the solid-state spectrum of this salt shows a high-energy band at 26.5 kK and a shoulder beyond 30 kK. The charge-transfer band is located at 11.6 kK. Although this value is coincident with that of K$^+$ *p*-Chloranil$^{\overline{\cdot}}$, the charge-transfer band for Na$^+$ *p*-Chloranil$^{\overline{\cdot}}$ was found to be very much intensified. In accordance with this view, the high-energy band at 23.3 kK for K$^+$ *p*-Chloranil$^{\overline{\cdot}}$ is shifted to the band at 26.5 kK for Na$^+$ *p*-Chloranil$^{\overline{\cdot}}$, which is, therefore, assigned to the shifted band of the ${}^2B_{3g}\rightarrow{}^2B_{1u}$ transition for the anion-radical monomer. The π-π transitions of the monomer will be perturbed in the field of the other anion-radicals when the anion-radicals come close enough together for the π orbitals to overlap.

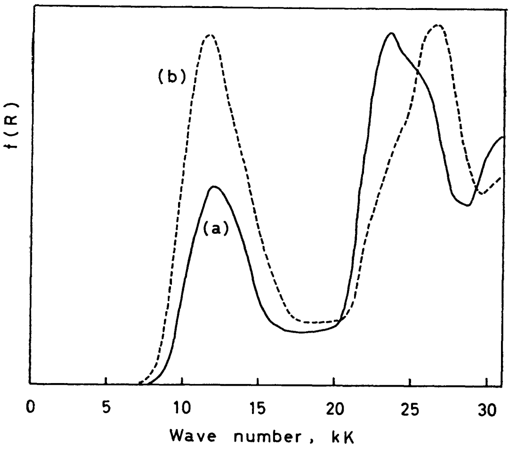

Fig. 3. The solid-state spectra of (a) K$^+$ *p*-Chloranil$^{\overline{\cdot}}$ and (b) Na$^+$ *p*-Chloranil$^{\overline{\cdot}}$.

K$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$ (Fig. 4, Curve a). Obviously, in spite of weak low-energy absorptions at 11.5 kK and at 17.4 kK, the solid-state spectrum of this salt is almost identical with that of the anion-radical monomer in an acetone solution. The strong band at 23.3 kK of the solid-state spectrum corresponds well to the ${}^2B_g\rightarrow{}^2A_u$ transition at 22.1 kK of the monomer spectrum. The shoulder around 30 kK of the solid salt corresponds to the place where the band at 30.2 kK appears in the monomer spectrum. The intensity of the charge-transfer band of this salt located at 11.5 kK is very much decreased in comparison with that at 11.8 kK of K$^+$ *p*-Chloranil$^{\overline{\cdot}}$. The origin of the other weak absorption, at 17.4 kK, of K$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$ remains in question. From the above-mentioned results, the anion-radicals in this salt appear to interact more weakly than those in K$^+$ *p*-Chloranil$^{\overline{\cdot}}$. It seems that the *p*-QBr_2Cl_2 anion-radicals exist almost as monomers in the solid state.

Na$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$ (Fig. 4, Curve b). Unlike K$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$, this salt shows strong absorptions at 12.2 kK and at 26.3 kK, and a slight shoulder around 22 kK. These features seem to be similar to those of Na$^+$ *p*-Chloranil$^{\overline{\cdot}}$. Figure 4 shows that the intensity of the charge-transfer band for Na$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$ is very much increased compared

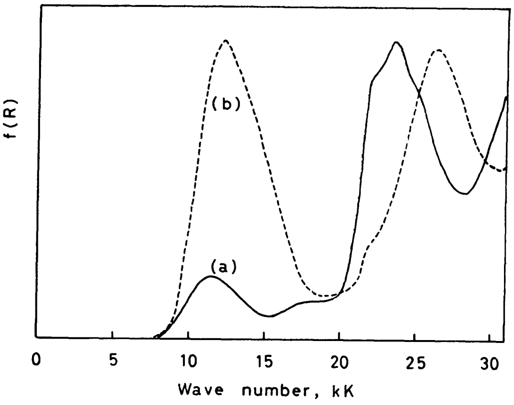

Fig. 4. The solid-state spectra of (a) K$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$ and (b) Na$^+$ *p*-$QBr_2Cl_2^{\overline{\cdot}}$.

to that for K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$. In accordance with this view, the band at 23.3 kK due to the $^2B_g \rightarrow {}^2A_u$ transition for K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$ is appreciably shifted to 26.3 kK for Na^+ p-$QBr_2Cl_2^{\overline{\cdot}}$. Judging from these results, the situation of the solid state of this salt seems to be very analogous to that of Na^+ p-Chloranil$^{\overline{\cdot}}$.

K^+ *p*-Bromanil$^{\overline{\cdot}}$ (Fig. 5, Curve a). The solid-state spectrum of this salt shows weak low-energy bands at 10.9 kK and at 17.5 kK, and a strong high-energy band at 23.0 kK. The locations of the band peaks for this salt coincide with those of K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$. The high-energy band at 23.0 kK corresponds well with the band due to the $^2B_{3g} \rightarrow {}^2B_{1u}$ transition at 22.2 kK for the p-bromanil anion-radical monomer. The intensity of the low-energy band is as weak as that of K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$. These spectroscopic features clearly indicate that the situations in these two substances are very much alike.

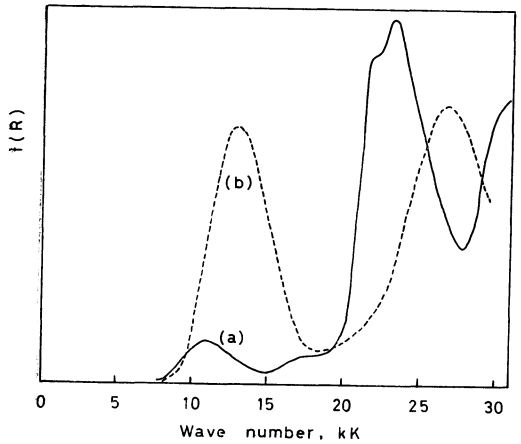

Fig. 5. The solid-state spectra of (a) K^+ p-Bromanil$^{\overline{\cdot}}$ and (b) Na^+ p-Bromanil$^{\overline{\cdot}}$.

Na^+ *p*-Bromanil$^{\overline{\cdot}}$ (Fig. 5, Curve b). Unlike K^+ p-Bromanil$^{\overline{\cdot}}$, this salt shows a solid-state spectrum comprising a strong band at 13.0 kK and a strong high-energy band at 26.8 kK. It is interesting to see that these spectral differences between Na^+ p-Bromanil$^{\overline{\cdot}}$ and K^+ p-Bromanil$^{\overline{\cdot}}$ are very analogous to those between Na^+ p-$QBr_2Cl_2^{\overline{\cdot}}$ and K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$. Therefore, the mode of the charge-transfer interaction in Na^+ p-Bromanil$^{\overline{\cdot}}$ seems to be very similar to that in Na^+ p-$QBr_2Cl_2^{\overline{\cdot}}$.

Discussion

The experimental results of the solid-state spectra clearly indicate that these anion-radical salts can be classified into the following three groups (this classification is based on the mode of the charge-transfer interaction between the anion-radical molecules):

(I) K^+ p-$QBr_2Cl_2^{\overline{\cdot}}$ and K^+ p-Bromanil$^{\overline{\cdot}}$ belong to this group, in which the solid-state spectra are almost identical with the spectrum of the anion-radical monomer. This means that the anion-radical molecules exist as monomers in the solid state. Hence, the magnetic properties of these salts may be expected to exhibit nearly the behaviour due to free-spin paramagnetism. In this case, the temperature variation of the paramagnetic susceptibility may be approximated by the Curie law.

(II) Na^+ p-Chloranil$^{\overline{\cdot}}$, Na^+ p-$QBr_2Cl_2^{\overline{\cdot}}$, and Na^+ p-Bromanil$^{\overline{\cdot}}$ belong to this group. In these cases, the intensity of the low-energy charge-transfer band is remarkably strong, and the high-energy band, originating from the monomer band, is blue-shifted. A strong charge-transfer interaction between the anion-radicals is expected to cause such behaviour. Therefore, the intermolecular overlap between the molecular orbitals of the anion-radicals is quite large in the crystal of these salts. For this reason, the anion-radicals seem to be stacked in the solid salts one flat upon another to form parallel chains. On the other hand, such a crystal system is considered to be a linear-chain antiferromagnet, since the charge-transfer interaction leads to a considerable stabilization of the state where the spins are antiparallel.[2-4] It can, therefore, be expected that the salts in this group may be diamagnetic or, at most, weakly paramagnetic at room temperature.

(III) Only K^+ p-Chloranil$^{\overline{\cdot}}$ belongs to this group. The spectrum of this salt shows a low-energy charge-transfer band. However, the high-energy band is similar to the monomer band. Therefore, the charge-transfer interaction for this group is intermediate between those for the (I) and (II) groups. Such an intermediate case may be observed only when the temperature of the measurement is comparable with the interaction. McConnell and Lynden-Bell have discussed the electronic structures for such systems composed of the linear chains of $S=1/2$ ion-radical molecules.[10] According to their discussion, at temperatures which are large compared to the exchange interaction, the spin of any one individual radical interacts equally strongly with two others, while at temperatures comparable to or less than the exchange interaction the linear chains are unstable with respect to the distortions that produce an alternation in the distances between the interacting units. At this time, since this effect is cooperative, a sharp decrease in the magnetic susceptibility may be expected. In accordance with this view, Andre *et al.* have found a sharp decrease in the paramagnetic susceptibility for K^+ p-Chloranil$^{\overline{\cdot}}$ around 250°K when the temperature is

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[10] H. M. McConnell and R. Lynden-Bell, *J. Chem. Phys.*, **36**, 2393 (1962).

lowered.[11] We consider that this "magnetic" anomaly may be attributed to the phase-transition that has been discussed by McConnell and Lynden-Bell.[*3]

Summarizing the above-mentioned results, we have to note that the charge-transfer interaction in these anion-radical salts is largely affected not only by the kinds of the halogen substituents in the anion-radical molecules, but also by the species of the counter cations. In the case of the potassium cation, the interaction of the salt is markedly decreased compared to that of the sodium salt. In this respect, the crystal structure of the potassium salt is expected to be quite different from that of the sodium salt. This difference may be related to the difference in the ion radii between these two cations. It is obvious that the charge-transfer interaction is decreased when the substituted chlorine for the anion-radical molecule is replaced by bromine.

In conclusion, the existence of charge-transfer interaction between ion-radical molecules is not limited to Würster cation-radical salts or TCNQ anion-radical salts, but is regarded as of the nature of ion (cation and anion) radical salts in general.

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11) J. J. Andre, J. Clementz, R. Jesser and G. Weill, *C. R. Acad. Sci. Paris*, **t. 266**, 1057 (1968).

[*3] Similar anomalies in the magnetic susceptibilities of ion-radical salts have previously been observed with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (Würster's Blue) perchlorate at 189°K and with $[(C_6H_5)_3PCH_3]^+$-$(TCNQ)_2^{-}$ at 315°K. See W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962); K. Okumura, *J. Phys. Soc. Japan*, **18**, 69 (1963); R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963); Y. Iida, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, **37**, 428 (1964).