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Infrared Spectra of Tribromochloro-*p*-benzoquinone and Its Anion Radical

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Synopsis. A chemically-stable anion radical salt of tribromochloro-*p*-benzoquinone was synthesized. The infrared spectrum of the anion radical was examined together with its neutral molecule.

The vibrational spectrum of an ion radical is known to differ distinctly from that of its neutral molecule.[1-8] So far, few quantitative studies have been made on such a difference. The infrared spectra of *p*-chloranil (*p*-QCl_4), *p*-bromanil (*p*-QBr_4), 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (*p*-QBr_2Cl_2) and their corresponding anion radicals were previously examined.[3-6] In order to explain the frequency difference in fundamental vibration between the neutral molecule and its anion radical, the fundamental frequencies were assigned, and the simple Urey-Bradley force fields were determined for both the neutral and anion radical molecules. We are able to understand these frequency differences on the basis of the difference in the intramolecular force fields of the two molecules. It was found that the force constants of *p*-QBr_2Cl_2 and its anion radical can be transferred from those of *p*-QX_4, (X= Cl or Br), and its anion radical, respectively.[6] Measurements of the infrared spectra (400—4000 cm^{-1}) of tribromochloro-*p*-benzoquinone (*p*-QBr_3Cl) and its anion radical have been carried out in order to observe the difference in the spectra of these neutral and anion radical molecules. The fundamental vibrations were assigned by comparison with those of *p*-QX_4, (X=Cl or Br), *p*-QBr_2Cl_2 and their anion radicals.

The neutral *p*-QBr_3Cl was prepared by the oxidation of tribromochlorohydroquinone and purified by recrystallization from benzene or gracial acetic acid. The anion radical salt with the potassium cation (K^+ *p*-QBr_3Cl^-), which is stable at room temperature, was synthesized by the method of Torrey and Hunter.[9] The infrared spectra of these solid compounds were measured as Nujol mulls in the range 400—4000 cm^{-1} with an IR-G infrared spectrophotometer (Japan Spectroscopic Co., Ltd.). The infrared spectra in the regions where the absorption due to Nujol appears were measured using hexachlorobutadiene mulls.

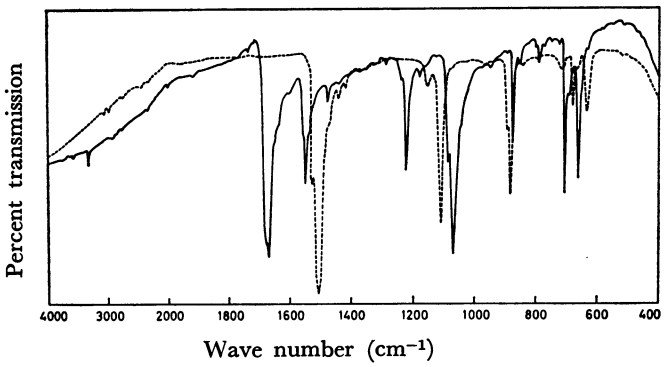

Fig. 1. The infrared spectra of neutral tribromochloro-*p*-benzoquinone (*p*-QBr_3Cl, ——) and its anion radical salt with the potassium cation (K^+ *p*-QBr_3Cl^-, ----).

The spectra obtained for these compounds are reproduced in Fig. 1. Since the counter cation of the anion radical salt is a simple alkali metal cation, the observed spectrum of K^+ *p*-QBr_3Cl^- in the region under investigation would be due to that of the *p*-QBr_3Cl anion radical itself. In the infrared spectra of the neutral *p*-QBr_3Cl and its anion radical, we can also observe appreciable frequency shifts between their corresponding bands. Although the point groups of these molecules are degraded into C_s, their spectroscopic features are found to be close to those of *p*-QX_4, (X=Cl or Br), *p*-QBr_2Cl_2 and their anion radicals,[3-6] where *p*-QX_4 and *p*-QBr_2Cl_2 have D_{2h} and C_{2h} point groups, respectively. Thus, the assignments of the fundamental vibrations of *p*-QBr_3Cl and its anion radical were made in comparison with those of symmetrical *p*-benzoquinones.

For the neutral *p*-QBr_3Cl, two strong absorptions at 1678 and 1671 cm^{-1} can definitely be assigned to the C=O bond stretching modes. For the anion radical, however, we could observe only one fundamental absorption due to the C=O mode at 1509 cm^{-1}, although there may appear two fundamentals from the symmetry property of the molecule. We note a remarkable red shift of 166 cm^{-1} upon introduction of an extra electron to the neutral *p*-QBr_3Cl. Such a large red shift has also been found in the cases of *p*-QX_4, (X=Cl or Br), *p*-QBr_2Cl_2 and their corresponding anion radicals.[3-6]

The strong absorption at 1551 cm^{-1} with shoulders for the neutral *p*-QBr_3Cl arises from the C=C bond stretching mode, the corresponding band for the anion radical being found at 1530 cm^{-1}. Thus, the fundamental absorption due to the C=C mode is red-shifted by 21 cm^{-1} when the neutral *p*-QBr_3Cl changes into its anion radical. On the other hand, the absorption at 1222 cm^{-1} of the neutral *p*-QBr_3Cl is attributable to the C–C bond stretching mode. The band at 1069 cm^{-1} with a shoulder at 1085 cm^{-1} of the same molecule may arise from the major contribution of the C–C bond stretching mode and the minor contribution of the C–Cl bond stretching mode. In comparison with the spectroscopic data of *p*-QX_4 (X=Cl or Br),[4,5] the bands at 1222 and 1069 cm^{-1} come mostly from the B_{3u} and B_{2u} modes of *p*-QX_4, respectively. This also implies the similarity of the spectroscopic features of *p*-QBr_3Cl and *p*-QX_4 (X=Cl or Br). As regards the corresponding absorption of the *p*-QBr_3Cl anion radical, only one fundamental absorption was observed at 1109 cm^{-1}. The band is attributable to a shifted band of 1069 cm^{-1} of the neutral *p*-QBr_3Cl, indicating an

appreciable blue shift by 40 cm^{-1} upon introduction of the extra electron to the neutral *p*-QBr_3Cl. According to previous experimental and theoretical investigations,[3-6] the C=C bond-stretching force constant decreases, while the C-C bond-stretching force constant increases, in going from the neutral *p*-QX_4 (X=Cl or Br) and *p*-QBr_2Cl_2 to their corresponding anion radicals. Such an increase of the C-C bond-stretching force constant leads to the blue shift of the 1109 cm^{-1} band of the *p*-QBr_3Cl anion radical. Although the 1222 cm^{-1} band of the neutral *p*-QBr_3Cl can also be expected to shift to higher energy region in its anion radical, no such absorption was observed in the anion radical presumably because of its weak intensity. The lack of this absorption of the C-C stretching mode has also been found in the series of the *p*-QX_4 (X=Cl or Br) and *p*-QBr_2Cl_2 anion radicals.[3-6]

In the wave number region 1000—400 cm^{-1}, the spectrum of the neutral *p*-QBr_3Cl has three strong absorptions at 876, 706, and 660 cm^{-1}, respectively. By referring to the assignments of *p*-QBr_4 and *p*-QBr_2Cl_2,[5,6] the 876 cm^{-1} band seems to arise from the mixing of the C-C, C-Cl, and C-Br bond-stretching modes, and the 660 cm^{-1} band from the mixing of the C-Cl and C-Br stretching modes.[10] On the other hand, the spectrum of the *p*-QBr_3Cl anion radical has three corresponding absorptions at 881 cm^{-1} with a shoulder around 891, at 682 and at 638, respectively.[10] The 881 cm^{-1} band shows a slight blue-shift, and the 638 cm^{-1} band a red-shift as compared to the corresponding 876 and 660 cm^{-1} absorptions of the neutral molecule. The C-Cl and C-Br bond-stretching force constants are known to be weakened by the formation of the anion radicals,[5,6] so that the appreciable red-shift of the 638 cm^{-1} band can be explained in terms of the mixing of the C-Cl and C-Br stretching modes. The reason for the slight blue-shift of the 881 cm^{-1} band is that it arises from the mixing of the C-C, C-Cl and C-Br stretching modes, and the C-C stretching force constant is strengthened by forming the anion radical.

In view of these results, although the molecular symmetries of the neutral *p*-QBr_3Cl and its anion radical are degraded from those symmetrical *p*-QX_4 (X=Cl or Br), *p*-QBr_2Cl_2 and their anion radicals, the spectroscopic features of *p*-QBr_3Cl and its anion radical can be understood on the basis of the infrared spectra reported on the symmetrical *p*-benzoquinones and their anion radicals.[3-6]

References

1) J. Stanley, D. Smith, B. Latimer, and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966).
2) Y. Matsunaga, *Nippon Kagaku Zasshi*, **89**, 905 (1968), and the references cited therein.
3) Y. Iida, *J. Phys. Soc. Jpn.*, **27**, 1371 (1969).
4) Y. Iida, *Bull. Chem. Soc. Jpn.*, **43**, 345 (1970).
5) Y. Iida, *Bull. Chem. Soc. Jpn.*, **46**, 2955 (1973).
6) Y. Iida, *Bull. Chem. Soc. Jpn.*, **47**, 99 (1974).
7) Y. Iida, *Bull. Chem. Soc. Jpn.*, **46**, 423 (1973).
8) J. J. Hinkel and J. P. Devlin, *J. Chem. Phys.*, **58**, 4750 (1973).
9) H. A. Torrey and W. H. Hunter, *J. Am. Chem. Soc.*, **34**, 702 (1912).
10) The 876 and 660 cm^{-1} bands of the neutral *p*-QBr_3Cl shift to the 869 and 650 cm^{-1} bands in the neutral *p*-QBr_4, respectively, while the 706 cm^{-1} band shows no such shift when the neutral *p*-QBr_3Cl changes into the neutral *p*-QBr_4. The absorptions at 881 cm^{-1} with a shoulder around 891 and at 638 of the *p*-QBr_3Cl anion radical shift to those at 879 and 618 cm^{-1} in the *p*-QBr_4 anion radical, respectively, while the 682 cm^{-1} band shows no such shift when the *p*-QBr_3Cl anion radical changes into the *p*-QBr_4 anion radical (see Ref. 5).