

## Infrared Spectroscopic Studies of Charge-Transfer

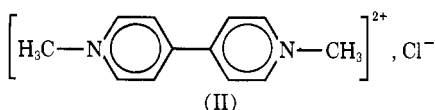
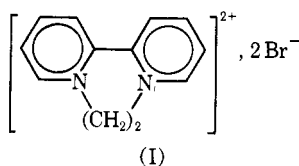
## Complexes of Diquat and Paraquat

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The formation of charge-transfer complexes between diquat or paraquat and halide ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) ions is reported by infrared spectroscopic technique. The vibrational frequency bands in diquat or paraquat depend on the nature of the anion ( $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ). The strong band at  $854\text{ cm}^{-1}$  in

paraquat dichloride and  $793\text{ cm}^{-1}$  in diquat dibromide, which were assigned to the umbrella mode, shifted to lower frequency with the decreasing electronegativity of the anion ( $\text{Cl}^-$  to  $\text{I}^-$ ). The results are compared with pyridinium halide complexes.

**D**iquat (I) and paraquat (II) are quaternary salts of substituted isomeric bipyridine and are used as herbicides (Boon, 1965). They readily form free radicals and charge-transfer complexes. Both free radical formation and charge-transfer complex (Haque *et al.*, 1969) have been discussed in connection with their biological activity. Recently, nuclear magnetic resonance (Haque *et al.*, 1969) and absorption spectrophotometry (Haque *et al.*, 1969; Nakahara and Wang, 1963) have been used to study the



structure of the halide charge-transfer complexes of paraquat and diquat. In this note we shall present evidence of charge-transfer complex formation of paraquat and diquat with halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) using an infrared technique.

## EXPERIMENTAL

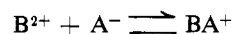
Diquat and paraquat used were of analytical grade and supplied by the Ortho Division of Chevron Chemical. All the other salts (KI, KBr, KCl) used were of reagent grade. The halide complexes were prepared by grinding (0.5 hr) excess potassium salt of the halide with paraquat dichloride or diquat dibromide. The mixture was then pressed (under 1500 lb pressure for) into a pellet for analysis. All the pellets were prepared under similar conditions. The color of diquat or paraquat was dependent on the nature of the anion, *i.e.*, changed to light yellow, bright yellow, and orange-brown for  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions, respectively, although this indicated an interaction between diquat or paraquat and the anion.

Spectra for the region  $4000\text{--}600\text{ cm}^{-1}$  were obtained on a Beckman IR-7 spectrometer (using NaCl optics). Spectra were recorded with varying thickness of the pellet to check the packing. However, the position of the vibration bands was not dependent on the thickness of the pellet.

## RESULTS AND DISCUSSION

The ir spectra of diquat and paraquat show vibration bands in three distinct regions:  $3200\text{--}2800\text{ cm}^{-1}$ ;  $1700\text{--}1100\text{ cm}^{-1}$ ; and  $1100\text{--}600\text{ cm}^{-1}$  (Figure 1). The vibration bands in the region  $3200\text{--}2800\text{ cm}^{-1}$  are due to C-H stretching from the aromatic ring, the methyl on paraquat and methylene on diquat. Ring breathing, C-C stretching, and in-plane C-H deformation modes are found in the region  $1700\text{--}1100\text{ cm}^{-1}$ . At the far region,  $1100\text{--}600\text{ cm}^{-1}$ , the bands could be assigned to C-C in-plane bending, C-C out-of-plane bending, and out-of-plane C-H deformation. Since C-C bending modes are weak, the strong absorption in the far region is assigned to the out-of-plane C-H deformation modes. Among all of the out-of-plane C-H deformation modes, the motion which produces the greatest dipole moment change and therefore the most intense band is the umbrella mode (Bellamy, 1955). The strong bands at  $854\text{ cm}^{-1}$  in paraquat dichloride and  $793\text{ cm}^{-1}$  in diquat dibromide are assigned to this mode.

Diquat or paraquat can dissociate according to the following equilibria:



where  $\text{B}^{2+}$  is the quaternary cation,  $\text{A}^-$  the anion, and  $\text{BA}^+$  and  $\text{BA}_2$  are the complexes.

Since the anion complexing effects the charge density on the ring, the vibrational bands in the ir spectra should shift when the anion is varied, especially the out-of-plane C-H deformation modes. This expected shift is observed for paraquat ion as the umbrella band shifts to  $815\text{ cm}^{-1}$  for bromide and  $810\text{ cm}^{-1}$  for iodide. The corresponding band in diquat is found at  $781\text{ cm}^{-1}$  for the iodide. The amount of charge transfer from the halide ion to the quaternary pyridinium ion should increase with decreasing electronegativity and the results show that this does occur. Similar

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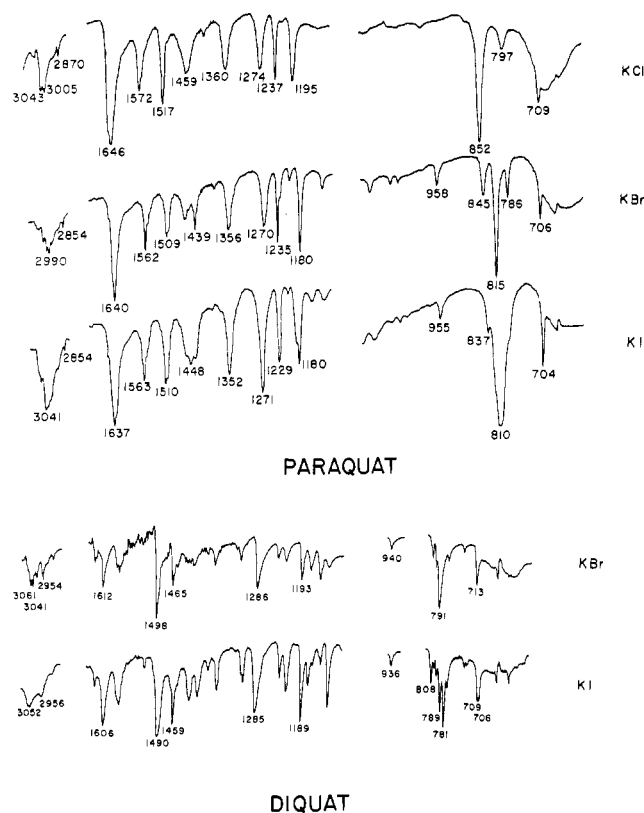


Figure 1. Infrared spectra of paraquat and diquat ions in various potassium halides

Table I. Changes in the Out-of-Plane C-H Deformation Mode of Paraquat and Diquat as a Function of Anions

Cation	Anion	Reduced mass <sup>a</sup>	Out-of-Plane C-H deformation mode frequency, cm <sup>-1</sup>
Diquat	Bromide	10.4	793
Diquat	Iodide	10.95	781
Diquat	Montmorillonite		782
Paraquat	Chloride	9.0	854
Paraquat	Bromide	10.4	815
Paraquat	Iodide	10.95	810
Paraquat	Montmorillonite		834

<sup>a</sup> Using carbon as the other atom.

changes in the vibration frequencies for pyridinium halide complexes have been observed by Cook (1961). The changes in the vibration bands can be explained by comparing these results with those of Kross *et al.* (1956). These workers observed shifts in the C-H out-of-plane bending vibration frequency in mono-substituted and para-disubstituted benzenes. The frequency of this vibration mode increased with increasing electrophilic nature of the substituent. The electrophilic nature of the substituents usually depletes the aromatic nucleus of  $\pi$ -electronic charge. This depletion of the  $\pi$ -electron density of the aromatic nucleus makes it difficult for the carbon bonding orbitals to follow the out-of-

plane movement of hydrogen atoms. Similar arguments can be used for the changes in the out-of-plane vibration frequencies of diquat and paraquat in the presence of halide ions. It may be possible that on charge-transfer complex formation the electronegative nature of the halide ions produces enough decrease in the  $\pi$ -electron density of the aromatic nucleus that it makes it difficult for the carbon bonding orbital to follow the hydrogen atoms in vibration. A similar relationship has been shown by Bellamy (1955) who established a correlation between frequencies of the out-of-plane deformation and Hammett's  $\sigma$  values for substituted aromatics. The results could also be compared with those of Cook (1961) on pyridinium ion charge-transfer complexes. Pyridinium ion showed characteristic changes in its vibrational frequencies with changes in the nature of the anion. The changes in the N-H stretching vibrations were quite significant and the out-of-plane hydrogen deformation frequencies of the pyridinium ion showed changes similar to those observed for diquat and paraquat. In all the cases the shifts in frequency were functions of the electronegativities of the anions. It is interesting to note that the frequency of the out-of-plane C-H vibration is dependent on the mass of the halide ion. Apparently the frequency of this vibration decreases with increasing atomic weight of the halide ion. A linear correlation has been suggested by Margoshes and Fassel (1955) between the out-of-plane C-H bending vibration and the reduced mass for compounds of type M (phenyl)<sub>n</sub>. With the limited number of available data for diquat and paraquat charge-transfer complexes, it is difficult to generalize such a relationship; nevertheless a rough correlation is apparent between the reduced mass and the frequency of the out-of-plane C-H vibration (Table I).

Since diquat and paraquat readily adsorb on soil and clay surfaces, these findings can be compared to the mechanism (Haque *et al.*, 1970) of the adsorption of these compounds on montmorillonite surface. Infrared and ultraviolet spectroscopic studies have revealed the formation of charge-transfer complex formation between the diquat or paraquat cation and montmorillonite. The changes in the out-of-plane C-H deformation modes of diquat and paraquat in the presence of various anions are given in Table I.

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- Bellamy, L. J., *J. Chem. Soc.* 2818 (1955).  
 Boon, W. R., *Chem. Ind.* 782 (1965).  
 Cook, D., *Can. J. Chem.* 39, 2009 (1961).  
 Haque, R., Coshow, W. R., Johnson, L. F., *J. Amer. Chem. Soc.* 91, 3822 (1969).  
 Haque, R., Lilley, S., Coshow, W. R., *J. Colloid Interfac. Sci.* 33, 185 (1970).  
 Kross, R. D., Fassel, V. A., Margoshes, M., *J. Amer. Chem. Soc.* 78, 1332 (1956).  
 Margoshes, M., Fassel, V. A., *Spectrochem. Acta* 7, 14 (1955).  
 Nakahara, A., Wang, J. H., *J. Phys. Chem.* 67, 496 (1963).

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