# Chemisorption of p-Benzoquinone on Evaporated, Ta-Doped NaF- and $BaF_2$-Films, as Detected by Infrared Absorption Spectra

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The infrared spectra of HCN and $CO_2$ adsorbed on alkali halides were reported by KOZIROVSKY and FOLMAN [1]. We studied the infrared spectrum of p-benzoquinone adsorbed from the vapor on various alkali- and alkaline earth halides, as LiF, NaF, NaCl, KBr, $BaF_2$ and $CaF_2$ (see HARTMANN and LUCHTERHAND [2]). The high surface area films were obtained by evaporating the halides from a tantalum-coil, similar to the method in Ref. [1, 2]. Evidence is presented for chemisorption of p-benzoquinone on certain halide films.

The spectra were recorded in the range from $2000\ cm^{-1} - 400\ cm^{-1}$ with the Perkin Elmer Infrared grating spectrophotometer Model 225. Only upon adsorption on NaF and $BaF_2$ the infrared absorption bands of p-benzoquinone change markedly in intensity and position (see Fig. 1). For the vibrational assignment of the observed frequencies in the adsorbed state, we also studied the infrared spectra of p-benzoquinone-$d_4$, p-benzoquinone-$^{18}O_2$ and tetra-fluoro-p-benzoquinone (fluoranil) adsorbed on NaF and $BaF_2$. From these studies we concluded that p-benzoquinone is chemisorbed on these two salts. As an example, upon chemisorption on NaF its intensive C=O-stretching band ($\nu_{13}$ in the assignment of BECKER et al. [3]) is shifted about $250\ cm^{-1}$, its C–C-stretching band ($\nu_{19}$) about $100\ cm^{-1}$, both to a smaller wavenumber. Upon chemisorption on $BaF_2$ only its C–C-stretching band ($\nu_{19}$) is shifted (about $100\ cm^{-1}$) to a smaller wavenumber.

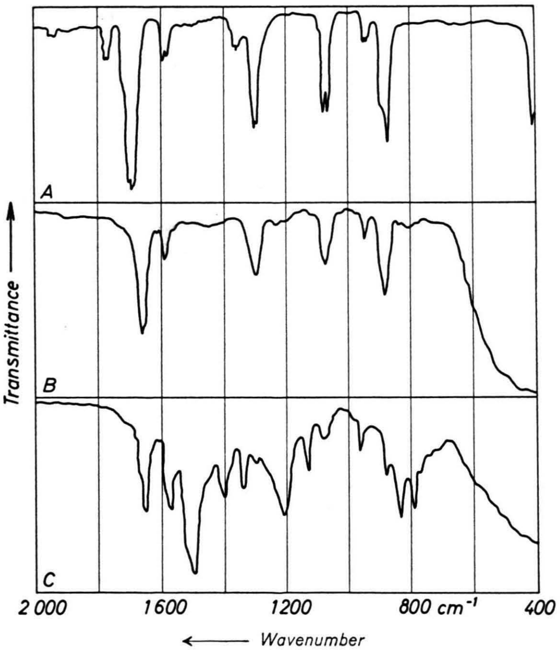

Fig. 1. Infrared Spectra of p-Benzoquinone, A) Vapor phase, Cell Temperature 60–120 °C, B) adsorbed on NaF(W), C) adsorbed on NaF(Ta).

Additional support for the given interpretation may be drawn from further spectroscopic results. The visible spectra of all four molecules chemisorbed on NaF show a broad absorption band with a maximum at 6300 Å; only fluoranil has an absorption band in the visible spectrum upon chemisorption on $BaF_2$, the maximum lying at 5200 Å. These bands are assigned as charge transfer bands, quinone being the acceptor. The EPR-spectrum of p-benzoquinone chemisorbed on NaF(Ta) (evaporated from a tantalum-coil) shows an intensive absorption band with a g-factor of around 2.

Upon adsorption of p-benzoquinone on tantalum-free NaF, which is obtained by evaporating NaF from a tungsten-coil [NaF(W)], the infrared spectrum does not change appreciably, in comparison to the vapor phase spectrum (see Fig. 1). For example the C=O-stretching band ($\nu_{13}$) is shifted about $25\ cm^{-1}$ to a smaller wavenumber, showing that p-benzoquinone is – without change in symmetry – physically adsorbed on NaF(W).

On evaporating NaF and $BaF_2$ from a tantalum-coil, the latter reacts with the fluorides, and tantalum is incorporated in the films of NaF and $BaF_2$. An analysis of evaporated NaF(Ta) showed the presence of 3000 ppm tantalum in the NaF film. We conclude, that the chemisorption of p-benzoquinone on NaF (and $BaF_2$) is an effect of the dotation of these salts with tantalum. It is possible to chemisorb also other substances on these doped salts.

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