

Chemisorption of p-Benzoquinone on Evaporated, Ta-Doped NaF- and BaF₂-Films, as Detected by Infrared Absorption Spectra

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The infrared spectra of HCN and CO₂ adsorbed on alkali halides were reported by KOZIROVSKY and FOLMAN¹. We studied the infrared spectrum of p-benzoquinone adsorbed from the vapor on various alkali- and alkaline earth halides, as LiF, NaF, NaCl, KBr, BaF₂ and CaF₂ (see HARTMANN and LUCHTERHAND²). 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 BaF₂ the infrared absorption bands of p-benzoquinone change markedly in intensity and position (see Fig. 1). For the vibrational assign-

ment of the observed frequencies in the adsorbed state, we also studied the infrared spectra of p-benzoquinone-d₄, p-benzoquinone-¹⁸O₂ and tetra-fluoro-p-benzoquinone (fluoranyl) adsorbed on NaF and BaF₂. 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 (ν_{13} in the assignment of BECKER et al.³) is shifted about 250 cm⁻¹, its C–C-stretching band (ν_{19}) about 100 cm⁻¹, both to a smaller wavenumber. Upon chemisorption on BaF₂ only its C–C-stretching band (ν_{19}) is shifted (about 100 cm⁻¹) to a smaller wavenumber.

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 fluoranyl has an absorption band in the visible spectrum upon chemisorption on BaF₂, 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 (ν_{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 BaF₂ from a tantalum-coil, the latter reacts with the fluorides, and tantalum is incorporated in the films of NaF and BaF₂. 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 BaF₂) 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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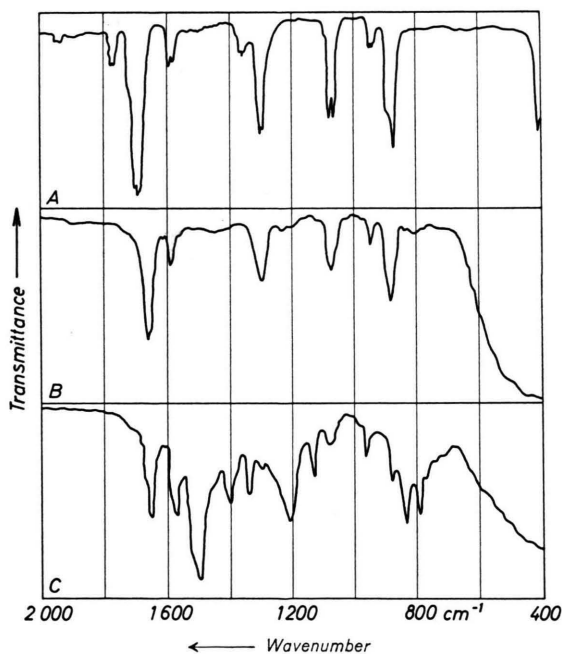


Fig. 1. Infrared Spectra of p-Benzoquinone, A) Vapor phase, Cell Temperature 60–120 °C, B) adsorbed on NaF(W), C) adsorbed on NaF(Ta).

¹ Y. KOZIROVSKY u. M. FOLMAN, J. Chem. Phys. **41**, 1509 [1964]; Trans. Faraday Soc. **62**, 1431 [1966].

² H. HARTMANN u. H. LUCHTERHAND, Z. Phys. Chemie, N. F. **46**, 103 [1965].

³ E. D. BECKER, E. CHARNEY, and T. ANNO, J. Chem. Phys. **42**, 942 [1965].