Preparation of *o*-Nitrosophenols from Benzene or Other Aromatic Hydrocarbons at Room Temperature

By Oskar Baudisch

Sodium pentacyano-ammine-ferroate (ammin salt) (2 g.) was dissolved in 100 cc. distilled water and 25 cc. of benzene as well as 50 cc. of ligroin added and the mixture cooled with ice water. Now 2 g. of $NH_2OH \cdot HCl$ is dissolved in the solution (color changes from brown to grass green) and 4 cc. of Merck superoxol added. (Color changes from grass green to deep brownish-violet.) Already, a few minutes after adding the hydrogen peroxide *o*-nitrosophenol can be detected in the ligroin layer. After shaking violently for one hour, the color of the benzene–ligroin layer is deep green, due to the formation of larger amounts of *o*-nitrosophenol. The green benzene–ligroin part (aqueous part P) is now separated, washed with ice water and shaken with dilute copper sulfate solution. A deep red water soluble *o*-nitrosophenol copper salt (Sol. C) is formed while the benzene–ligroin becomes entirely colorless and is used for further extraction of the aqueous part P. After shaking for one or two hours the deep green benzene–ligroin is again separated and *o*-nitrosophenol converted into the red copper salt (Sol. C). The aqueous part is now diluted with 100 cc. of water and several times extracted with ligroin until the ligroin is only pale green in color. The copper salt solutions C, C_1, etc., are united, and in presence of petrol ether acidified with hydrochloric acid. The deep green petrol ether is washed with ice water free from excess acid. It keeps protected from light in the cold for weeks unchanged.

If benzene is replaced by toluene, ethylbenzene, xylene, phenylacetylene, chloro- or bromobenzene, similar results are obtained but with varying yields.

Sodium pentacyano-ammine ferroate can, however, not be replaced by ordinary ionized iron salts. In repeating the described experiment with ferrous sulfate (2 g.) only traces of *o*-nitrosophenol are formed.

In the complex sodium pentacyano-aquo-ferroate, which is formed from the ammin salt in the acid medium, the sixth free valence of the ferrous central atom shows an exceptionally great chemical affinity to NO compounds. This fact seems to be the main reason that the short-lived nitrosyl radical NOH is captured and brought into chemical reaction with inserted ethylene groupings.[1]

[1] *Science*, vol. No. 2389, 336 (1940).

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Raman Spectrum of an Aqueous Solution of Potassium Cyanate[1]

By Forrest F. Cleveland

In a recent investigation of the infrared absorption spectrum of a saturated aqueous solution of potassium cyanate, Williams[2] found intense bands for the freshly prepared solution at 870 and 2170 cm.$^{-1}$ which were attributed to fundamentals ν_1 and ν_3, respectively, of the linear $O—C{\equiv}N^-$ group. After the solution had stood for several days, additional absorption bands were observed at 1350, 1690 and 2860 cm.$^{-1}$. These bands were attributed to absorption by ammonium and carbonate groups formed by hydrolysis. The present note is a report of a Raman spectra study undertaken to supplement the infrared data.

Experimental

Ten cc. of an approximately saturated solution of "c. p. Baker's Analyzed" potassium cyanate was prepared and a one hour exposure made immediately. Following this a polarization spectrogram was made and the solution stored in a closed test-tube. One hour exposures were made on successive days over a ten day period and finally a polarization spectrogram of the aged solution was made.

Details regarding the experimental technique have been given in previous papers.[3] The 4358 Å. mercury line was used for excitation of the spectra.

Results

The results are summarized in Table I. Columns one, two and three give the Raman displacements in cm.$^{-1}$, estimated intensities and depolarization factors for lines in the spectrum of the fresh solution, while columns four, five and six give the corresponding data for the aged solution.

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[1] Presented at the Seattle, Washington meeting of the American Physical Society, June 21, 1940.

[2] Dudley Williams, This Journal, **62**, 2442 (1940).

[3] Forrest F. Cleveland and M. J. Murray, *J. Chem. Phys.*, **7**, 396 (1939); M. J. Murray and Forrest F. Cleveland, This Journal, **61**, 3546 (1939).