## 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-aquoferroate, 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 $\nu_1$ and $\nu_3$, 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).

TABLE I

RAMAN SPECTRA OF FRESH AND AGED POTASSIUM CYANATE SOLUTION

| Fresh Solution |  |  | Aged Solution |  |  |
|---|---|---|---|---|---|
| $\Delta\nu$ | $I$ | $\rho$ | $\Delta\nu$ | $I$ | $\rho$ |
| .. | .. | ... | 1003 | 8 | 0.4 |
| .. | .. | ... | 1033 | 8 | .3 |
| .. | .. | ... | 1064 | 10 | .3 |
| 1225 | 4 | 0.6 | .. | .. | ... |
| 1315 | 6 | .6 | .. | .. | ... |
| 2171 | 10 | .3 | .. | .. | ... |

In the spectrogram made on the third day, the lines observed for the fresh solution had disappeared and three new lines slightly above 1000 cm.$^{-1}$ had appeared. In addition, the solution which originally had been odorless had acquired the odor of ammonia. Observance of $NH_4^+$ lines was impossible because of the strong continuous background in that region.

## Discussion

Goubeau[4] found a weak line at 857, a very weak, questionable line at 970 and a line of medium intensity at 2192 cm.$^{-1}$ in the Raman spectrum of solid potassium cyanate. In aqueous solution, he found 852, very weak, and 2185, weak. Pal and Sen Gupta[5] also reported frequencies at 838 and 2183, and in addition listed frequencies at 1229 and 1314, not found by Goubeau. These two frequencies were found also in the present investigation.

As Williams points out, these lines cannot be attributed to vibrations of the linear $O—C\equiv N^-$ group. The fact that Goubeau found lines at 1204 (weak) and 1307 (strong) for cyanic acid suggests the possibility that there may be some of this acid in the potassium cyanate solution. Another possibility is that mercury cyanate or silver cyanate may have been present as an impurity. Goubeau found lines at 1232 (weak) and 1302 (medium) for the former and at 1233 (weak) and 1297 (medium) for the latter. He attributed these frequencies to the doublet $\nu_1$, 2 $\nu_2$ (analogous to the resonance doublet in carbon dioxide) of the linear $O=C=N^-$ group.

Aqueous solutions of potassium carbonate and potassium bicarbonate have Raman frequencies at 1069 and 1035 cm.$^{-1}$, respectively.[6] Measurements of the Raman spectra of aqueous solutions of ammonium carbonate and ammonium bicarbonate, for which no data were found in the literature, gave 1020(6)0.1 and 1007(4)0.3, respectively. These data suggest the origins of the lines observed at 1003, 1033 and 1064 in the spectrum of the aged potassium cyanate solution.

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[4] J. Goubeau, *Ber.*, **68**, 912 (1935).

[5] N. N. Pal and P. N. Sen Gupta, *Ind. J. Phys.*, **5**, 11 (1930).

[6] M. Magat, "Tables Annuelles de Constantes et Données Numériques, Effet Raman," Volume XII, Hermann & Cie., Paris, 1937.

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## Some Tertiary Amides of Adipic, Azelaic and Sebacic Acids

BY REYNOLD C. FUSON, JOHN W. ROBINSON, JR., AND LYELL C. BEHR

Tertiary amides have been studied but little and those of the higher acids scarcely at all. From the standpoint of solubility and basicity, this type of amide is of especial interest in connection with the theory of hydrogen bonding. Primary and secondary amides, being able to serve at once as donors and as acceptors, are associated in solution.[1] They have, accordingly, lower solubility in water than that to be expected for the monomeric form. Tertiary amides cannot associate through hydrogen bonding and hence do not share this abnormality.[2] Striking examples of these differences have been encountered with certain tertiary amides of adipic, azelaic and sebacic acids, prepared in connection with the synthesis of diketones by the Beis[3] method. The amides of this group are particularly interesting because solubility predictions based on structure place them near the borderline between so-called water-soluble and water-insoluble compounds.[4] That the primary and secondary amides fall in the latter group is evidence that they are associated.

The new amides were made by the interaction of acid chlorides with suitable secondary amines according to the general procedure of Maxim[5] and Montagne.[6] They proved to be water-soluble and were sufficiently basic to form hydrochlorides, chloroplatinates and chloroaurates.

## Experimental

**N,N,N',N'-Tetraethyladipamide** was made from diethylamine and adipyl chloride. After three recrystallizations from low-boiling petroleum ether, it melted at 52.5–53.5°.

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[1] Meldrum and Turner, *J. Chem. Soc.*, **93**, 876 (1908); **97**, 1605, 1805 (1910); von Auwers, *Ber.*, **70**, 964 (1937).

[2] Chaplin and Hunter, *J. Chem. Soc.*, 1114 (1937); 1034 (1938).

[3] Beis, *Compt. rend.*, **137**, 575 (1903).

[4] Shriner and Fuson, "Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., (1940, p. 10.

[5] Maxim, *Ann. chim.*, [10] **9**, 58 (1928).

[6] Montagne, *ibid.*, [10] **13**, 40 (1930).