Effect of Deuterium Substitution on Color

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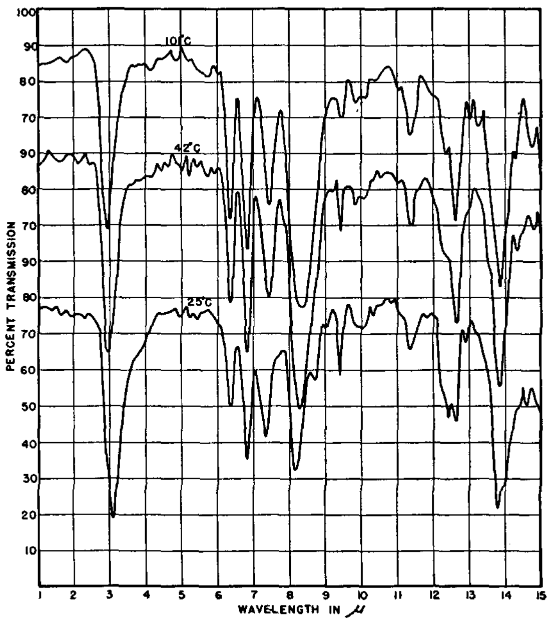

FIG. 1. The transmission spectra of phenol at various temperatures. Cell thickness approximately 0.01 mm.

and the fact that bands at approximately this wave-length are found in the spectra of a large number of compounds containing OH constitute evidence that this band is connected with the hydroxyl group.

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* In collaboration with Research Department, Calco Chemical Co. Inc.
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Effect of Deuterium Substitution on Color*

Although it is well known that substitution of a deuterium for a hydrogen atom in a compound modifies the physical properties of the compound, still there is no case recorded in the literature where such a substitution changes the color of the compound. Such a color change has been observed by us with nitroethane under special conditions.

When an equivalent quantity of $Ba(OD)_2$ is added to about $0.02N$ proto-nitroethane in heavy water, a proton is removed from the nitroethane to yield the ion $CH_3CH=NO_2^-$ according to the equation:

$$2CH_3CH_2NO_2+Ba^{++}+2OD^- = 2CH_3CH=NO_2^-+Ba^{++}+2HOD. \quad (1)$$

If to this solution be added now an equivalent quantity of D_2SO_4, a deuteron is reintroduced into the nitroethane to yield:

$$2CH_3CH=NO_2^-+Ba^{++}+D_2SO_4 = 2CH_3CHDNO_2+BaSO_4\downarrow. \quad (2)$$

Throughout these operations the solution remains perfectly colorless.

However, if an equivalent quantity of $Ba(OD)_2$ be again added, the solution turns *light yellow* very rapidly. In this case the reaction involved is:[1]

$$2CH_3CHDNO_2+Ba^{++}+2OD^- = 2CH_3CD=NO_2^-+Ba^{++}+2HOD. \quad (3)$$

The color can be discharged and brought back by repeated alternate additions of D_2SO_4 and $Ba(OD)_2$.

These same operations with $CH_3CH_2NO_2$ in light water and with $Ba(OH)_2$ and H_2SO_4 yield no colored solutions.

It will be observed that the only difference between the products in Eq. (1), where there is no color, and Eq. (3), where the yellow color appears, is in the nitroethane ion. In the former the ion is $CH_3CH=NO_2^-$, while in the latter it is $CH_3CD=NO_2^-$, the difference being in the substitution of a deuterium for a hydrogen atom on the carbon α to the nitro group.

From these observations in both H_2O and D_2O it can be concluded that $CH_3CH_2NO_2$, CH_3CHDNO_2, $CH_3CD_2NO_2$ and $CH_3CH=NO_2^-$ are colorless, while the ion $CH_3CD=NO_2^-$ is colored a light yellow in solutions about $0.02N$ with respect to nitroethane. Preliminary absorption measurements indicate that absorption starts at 5000–5200A and continues into the ultraviolet.

Because of the possible connection between the development of color and ease of proton and deuteron transfer in conjunction with acid-base catalysis and acid strength ultraviolet and visible absorption spectra are being investigated.

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