important difference 2 $(y - y_2)$ between the heat of formation of 2 single linkages, C–C, and of the double one, C=C. This difference, due to the change of constitution of the hydrocarbons examined, varies within the very large limits +8.0 cal. to +1.0 cal. In special cases it is possible that $2(y - y_2)$ can be equal to zero (for example, in naphthalene).

All of these computations are based on the newly corrected, very exact measurements, accumulated by only one investigator, P. W. Zubow.

The values of thermochemical characteristics can at present be considered as rough material for further mathematical elaboration of theories of valence.

WARSAW, POLAND.

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[THIRTIETH CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

# "THE ABSORPTION SPECTRA OF THE NITRIC ESTERS OF GLYCEROL."

BY ELLIOT QUINCY ADAMS.

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Hepworth,[1] from a study of the absorption spectra of the nitric esters of glycerol, concludes that it is evident that:

"(1) The labile and stable forms of nitroglycerin are physical isomerides, and both forms are identical in aqueous solution.

"(2) Commercial nitroglycerin is more absorptive than pure nitroglycerin.

"(3) The order of increasing absorption in aqueous solution is β-mononitrate, α-mononitrate, α,γ-dinitrate, α,β-dinitrate, and tri-nitrate.

"(4) α-Methylin[2] dinitrate is rather more absorptive than glycerol α,β-dinitrate.

"(5) The displacement of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro group produces a much more profound change in the absorption spectrum than the displacement of one or both hydrogen atoms of the remaining hydroxyl groups.

"(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro groups and the degree of absorption for any particular dilution."

The absorption spectra are given in 3 plots of the logarithm of the relative thickness in mm. of 0.00005 $N$ aqueous solution against the oscillation frequency.[3]

To determine whether there is any proportionality between the number of nitrate radicals and the absorption, it is necessary first to consider

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[1] Harry Hepworth, *J. Chem. Soc.*, 115, 840–7 (1919).

[2] α-Methylin is glycerol α-methyl ether. The parts of the summary in fine print are not referred to again in this paper.

[3] In the scales of logarithms a decimal point has been omitted. It is fairly evident that the standard concentration is 1/20,000 *gram molecular*. The oscillation frequency is the reciprocal of the wave length in mm.

what relation is to be expected. A solution showing the normal relation between concentration and absorptive power is said to obey Beer's Law, if the product of concentration and thickness of layer be kept constant, the absorption will remain the same. For such a solution the logarithm of the ratio of incident to transmitted light divided by the concentration and by the thickness gives a constant, known as the "specific extinction coefficient" or the "molecular extinction coefficient" according, respectively, as the concentration is in grams per liter or mols per liter. A fair comparison of substances of different molecular weight requires the use of the molecular extinction coefficient, or of some quantity proportional to it. To obtain such a value for the *relative molecular extinction coefficient*, or more briefly the absorptive power, from the plots of Hepworth, the intercepts of the ordinates for oscillation frequencies $\nu = 4200$ mm.$^{-1}$ (reciprocal millimeters) and $\nu = 4300$ mm.$^{-1}$ between the several curves and the top lines of the plots (log relative thickness = 4) have been read and the numbers corresponding to these logarithms recorded in Table I as $A_\nu/C$.

The "calculated" values of the absorptive power assume equal effect for each nitrate radical, and have been obtained by taking at each oscillation frequency $^1/_9$, $^2/_9$, and $^1/_3$, respectively, of the sum of the absorptions of the 5 nitrates. It will be seen that the agreement is all that can be expected until account is taken of the difference between isomers.

TABLE I.—RELATIVE MOLECULAR EXTINCTION COEFFICIENTS.

| Designation according to | | | $\nu = 4200$ mm.$^{-1}$. | | | $\nu = 4300$ mm.$^{-1}$. | | | Mean.[c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| Will. | Adams. | | log.[a] | $A\nu/C$. | Calc.[b] | log.[a] | $A\nu/C$. | Calc.[b] | $A\nu/C$. | Calc.[d] |
| - | - | Glycerol | [$-\infty$] | 0 | 0 | [$-\infty$] | 0 | 0 | 0 | 0 |
| β- | α- | Mononitrate | 0.18 | 1.5 | 1.7 | 0.62 | 4.2 | 4.2 | 2.8 | 2.5 |
| α- | β- | Mononitrate | 0.30 | 2.0 | | 0.74 | 5.5 | | 3.8 | 3.8 |
| αγ- | αγ- | Dinitrate | 0.39 | 2.5 | 3.3 | 0.84 | 6.9 | 8.5 | 4.7 | 5.0 |
| αβ- | αβ- | Dinitrate | 0.54 | 3.5 | | 0.95 | 8.9 | | 6.2 | 6.2 |
| αβγ- | αβγ- | Trinitrate | 0.74 | 5.5 | 5.0 | 1.10 | 12.6 | 12.7 | 9.0 | 8.8 |

[a] Obtained by reading down from top line of plots of Hepworth, *loc. cit.*, p. 842. The succession of integers and half-integers at $\nu = 4200$ mm.$^{-1}$ suggests that readings were taken at this oscillation frequency (among others) and with an accuracy of 0.5 unit of the (arbitrary) scale of relative absorptive power (relative molecular extinction coefficient).

[b] Assuming equal effect for each nitrate radical; this is, of course, only a first approximation.

[c] Since the experimental error in such measurements is considerable, the final comparison is made on the mean of the 2 absorption values.

[d] Assuming 2.5 for the effect of a nitrate radical in $\alpha(=\gamma)$ position and 3.75 for one in the β-position. See Figs. 1 and 2.

The difference between isomers is most simply explained as due to the difference in the absorptive effect of a nitrate radical according as its attachment to carbon is primary or secondary. As the designations

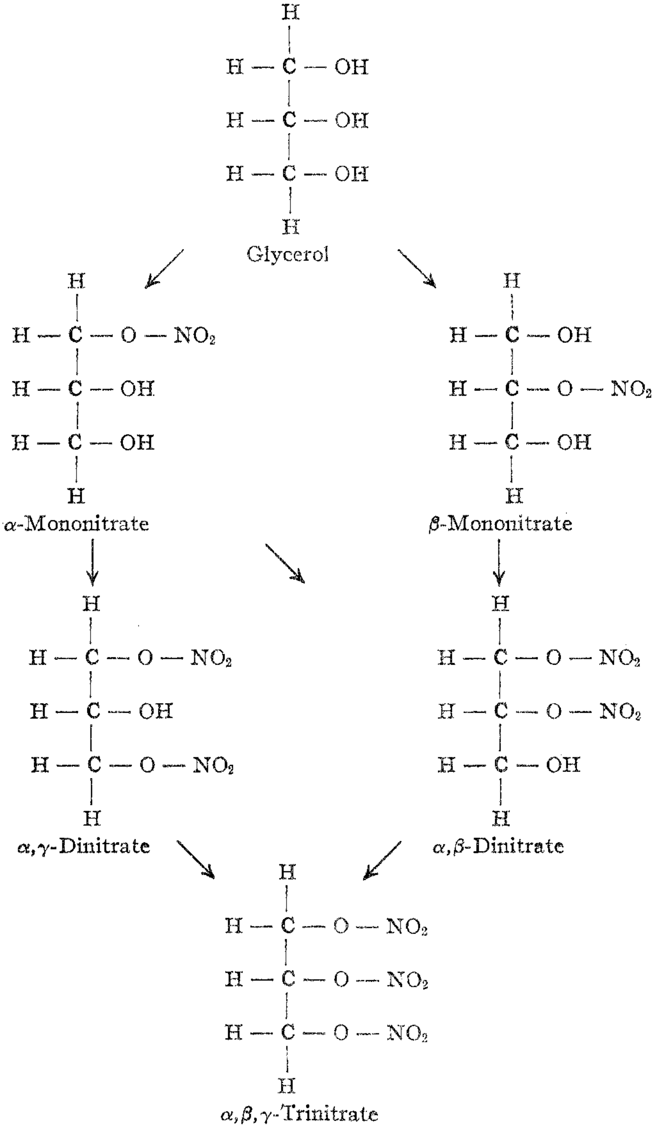

Fig. 1.

for the isomers, as given by Hepworth, are not compatible with such an explanation, it will be well to examine the evidence for those designations.

Hepworth (*loc. cit.*) gives no evidence for the designations, other than that given by the work of Nef[1] and Will.[2] Nef prepared "Glycidnitrat"

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[1] J. U. Nef, "Dissociationsvorgänge in der Glycol-Glycerinreihe," *Ann.*, 335, 238 (1904).

[2] W. Will, "Über Glycerin-nitrate," *Ber.*, 41, 1107–25 (1908).

by the interaction of epi-iodohydrin and silver nitrate. This substance, on heating with water at 100°, gave an oil easily soluble in water and ether, "welches wohl α-Mono-nitroglycerin darstellt." Will prepared the entire series of nitrates and established their composition by the analysis of their derivatives, particularly the nitrobenzoyl esters. He inferred the constitution of the isomeric mono- and dinitrates from the products resulting from the further nitration of the mononitrates (see Fig. 1), the mononitrate from which 2 dinitrates were obtained being called α, and that from which only one dinitrate resulted, β. Since mixed melting point observations prove the identity of his α-mononitrate with that prepared by the method of Nef, the results of these two investigators agree, and both must be accounted for before any change can be made in the designations of the mononitrates.

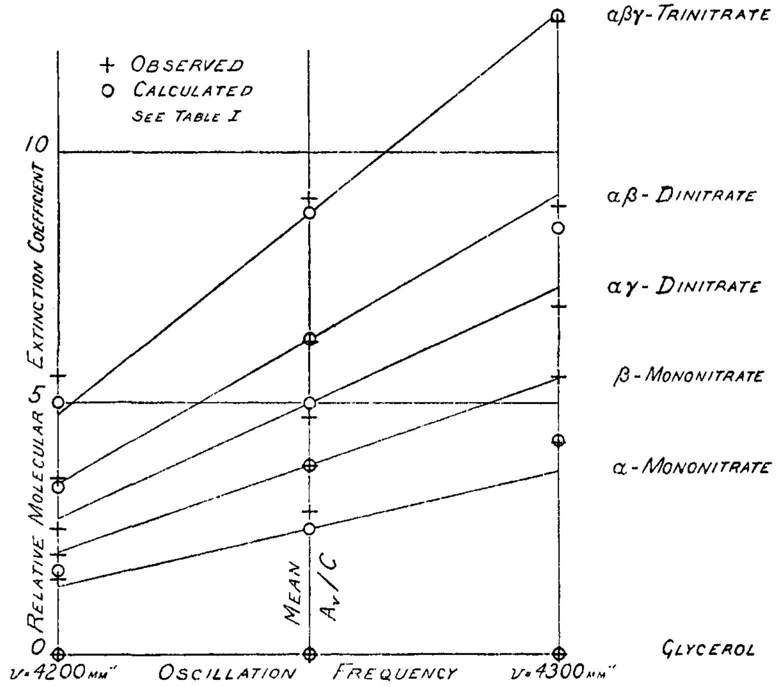

Fig. 2.

Will states[1] "In the investigation of the nitration it is further shown that the β-mononitrate is more readily nitrated to the trinitrate than is the α-mononitrate. By cautious nitration to the dinitrate the β-mononitroglycerin does not furnish both dinitroglycerins, as the mononitrate melting at 58° does, but it was possible to obtain only one such, namely,

[1] *Loc. cit.*, pp. 1119, 1121. In one case conc. nitric acid, sp. gr. 1.52, was used; in the other dilute acid (20% $H_2O$).

the dinitrate designated above as dinitroglycerin F." The trinitrate was formed also in both cases. The significance of this marked difference in ease of nitration must be considered further.

Differences in the rates of nitration of the various mono- and dinitrates will be due to 2 factors, an intrinsic difference in the reactivity of hydroxyls in the α- and β-position, and the steric effect of the nitrate radicals already present. These may act in 2 ways, they may, by their size or mass, decrease the reactivity of neighboring groups, the familiar "steric hindrance;" and they may be so situated as to render the molecule optically active. Since nitric acid is a substance optically inactive, and since in no case do enantiomorphs behave differently with inactive reagents, there is no reason to expect the possibility or impossibility of optical activity to have any effect on the rate of nitration. If the α-hydroxyl were the reactive one, no great difference in the reactivity of the two mononitrates should be expected (see Fig. 1), since both have at least one such hydroxyl, and the steric hindrance will be less in the case of the α-mononitrate which has only one. If, on the other hand, the β-hydroxyl is the more reactive, the α-mononitrate, which has it, should be appreciably more reactive.

On the basis of this assumption the following behavior with dil. nitric acid is to be expected with the β-mononitrate little or no action, since it has only unreactive hydroxyls blocked by an adjacent nitrate radical; with the α-mononitrate the principal product, by replacement of the reactive hydroxyl, will be the α,β-dinitrate which will not react further, but the unblocked α-hydroxyl may be expected to react to some extent, giving the α,γ-dinitrate, the reactive β-hydroxyl of which will be replaced to give the trinitrate. This agrees in all details with the *results* of Will,[1] but requires a reversal of his designations α- and β- for the mononitrates.

The relatively unreactive β-mononitrate, on treatment with conc. nitric acid would give in the first instance the α,β-dinitrate, by the further nitration of that compound the trinitrate; the rise in temperature resulting from the dilution of the excess of conc. nitric acid with water[2] would cause a partial hydrolysis of the trinitrate to give the α,γ-dinitrate; hence the ether extract of the resulting solution will contain (as Will found) both dinitrates and some trinitrate.

It remains to account for the production of the β-mononitrate by the method of Nef from "glycidnitrat,"[3] by the action of boiling water. By reference to Fig. 3 it will be seen that "glycidnitrat" contains 2 particularly reactive groups; an ethylene oxide ring and a double bond. If a

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[1] W. Will, "Das α-mononitrat schied, unter gleichen Bedingungen nitriert, überhaupt kein Öl ab," *loc. cit.*, p. 1121.

[2] W. Will, *loc. cit.*, p. 1119.

[3] J. U. Nef, "Glycid is γ-hydroxy-propylene oxide," *loc. cit.*

rearrangement occurs, there would be formed glyceryl orthonitrate[1] which, by the addition of water, could give either mononitrate. Again, "glycidnitrat" is insoluble in water; hydrolysis to "glycid" and nitric acid would permit it to go into solution. In a subsequent addition of nitric acid to the ethylene oxide ring the negative nitrate radical would be expected, by analogy to additions to unsaturated hydrocarbons, to add to the $\beta$-carbon atom. Finally, if the "glycid" should first hydrate to glycerol, the nitration of this, according to the results of Will,[2] should

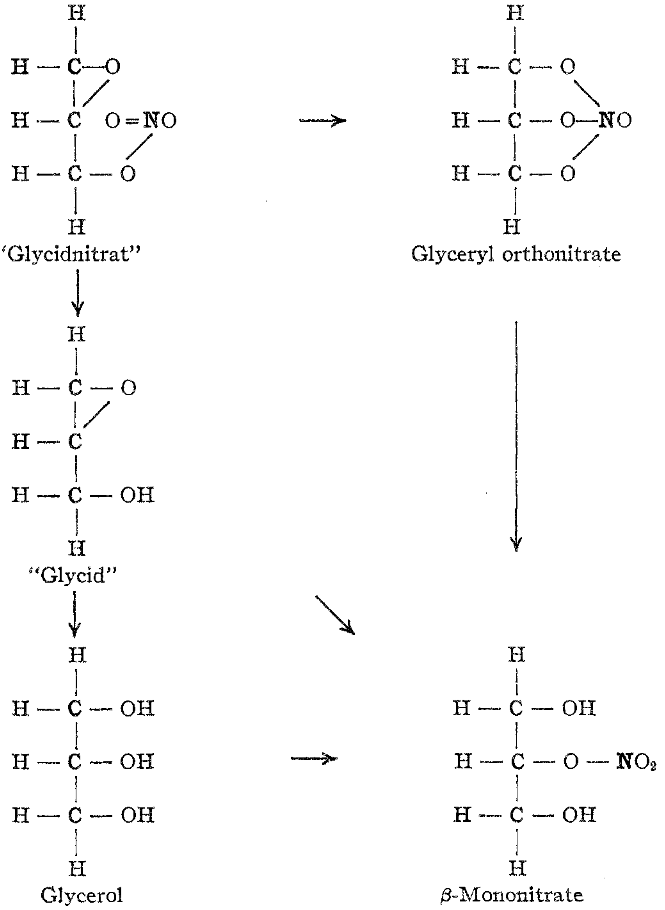

Fig. 3.

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[1] Orthonitrates have not been described. Orthophosphates and orthosilicates are well known; orthocarbonates are unknown as salts but have been prepared as esters, and by analogy the same should be true of the orthonitrates.

[2] W. Will, *loc. cit.*, p. 1121. It should be borne in mind that Will's use of the prefixes $\alpha$- and $\beta$- is exactly the reverse of that in the text above, as concerning the substances designated; in both cases it signifies the structure assigned to the compounds.

give a product 96–97% of which would be the same β-mononitrate. While no one of these reactions is proved to occur, the formation of a mononitrate from "nitroglycid" cannot be said to prove that it is the α-mononitrate when it is possible to account for the production of the β-mononitrate in 3 different ways.

To return to a consideration of the relation between constitution and absorptive power; the last two columns of Table I compare the mean of the absorptions observed at $\nu = 4200$ mm.$^{-1}$ and $\nu = 4300$ mm.$^{-1}$ with values calculated, assuming that each "primary" nitrate radical contributes 2.5 to the mean relative absorptive power, and each "secondary" nitrate radical 3.75.[1] The agreement between the absorptions observed and calculated is well within the probable error (about 0.35 unit).

## Summary.

1. In plotting absorption spectra the use of the *logarithm* of the specific (or molecular) extinction coefficient should be avoided, since it tends to obscure the relation between constitution and absorption.

2. The designations α- and β- applied by Will[2] to the two mononitrates derived from glycerol, should be interchanged.

3. It is possible that the "glycidnitrat" described by Nef[3] is glyceryl orthonitrate.

4. The absorption spectra of the nitric esters of glycerol, as given by Hepworth,[4] can be completely accounted for on the assumption that each nitrate radical has an absorptive effect dependent upon its location in the molecule, but independent of the presence or absence of other nitrate radicals.

5. The absorptive effect of the nitrate radical is about 1.5 times as great when it replaces the β-hydroxyl of glycerol as when it replaces an α-hydroxyl.

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[1] The accuracy of the data does not warrant expressing these numbers to better than quarter-units. The ratio of 2 : 3 between them is accidental.

[2] W. Will, "Über Glycerin-nitrate," *Ber.*, 41, 1107–25 (1908).

[3] J. U. Nef, *Ann.*, 335, 238 (1904).

[4] Harry Hepworth, *J. Chem. Soc.*, 115, 840–7 (1919).