which may be assumed to consist of one molecule of aureomycin hydrochloride.[3]

We have been unable to obtain crystals of the free base in a size suitable for single crystal work. We have likewise been unsuccessful in our efforts to obtain suitable crystals of the hydrobromide, hydroiodide and chloroplatinate of aureomycin.

Crystal modifications other than those described above have been observed both for bromamphenicol and aureomycin hydrochloride but these have not been extensively studied.

We are indebted to Parke, Davis and Co. for samples of chloramphenicol and bromamphenicol, and also for much helpful information, and to the Lederle Laboratories for a sample of aureomycin hydrochloride. This investigation was aided by a grant from the National Foundation for Infantile Paralysis.

(3) Our value, 515, for the molecular weight of aureomycin hydrochloride is not in agreement with the molecular weight, 508, obtained by Broschard, *et al.*, (*Science*, **109**, 199 (1949)) for the free base. Broschard, *et al.*, also give analysis figures for the free base and hydrochloride; those for the free base contain an obvious error in that the oxygen percentage (by difference) should be 27.17 rather than 21.17. Taking this error into account, one may calculate $C_{33}H_{37}N_3O_8Cl$ for the free base, and $C_{33}H_{38}N_3O_8Cl_2$ for the hydrochloride. The molecular weight corresponding to the above empirical formula for the hydrochloride is 531.

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Preferential Complexing of Iron(III) with β-Glucose[1]

BY JOSEPH C. DELANEY,[2] JACOB KLEINBERG AND W. J. ARGERSINGER, JR.

During the course of investigations concerning iron(III) complex ions with glucose, a study was made of the effect of the presence of ferric chloride solution on the mutarotation of α-glucose. It was thought that any complex formation involved might produce a change in the rate of mutarotation of the sugar.

A weighed quantity of α-glucose, prepared according to the method of Hudson and Dale,[3] was dissolved in a known volume of 0.1 *M* hydrochloric acid, and the rate of mutarotation of the solution was observed. An equal amount of the same glucose sample was dissolved in 0.1 *M* hydrochloric acid which was 0.2 *M* with respect to ferric chloride, and the rotation was again measured as a function of time. The volumes of the two solutions were approximately equal; the *p*H values were the same. The polarimeter tube and the solutions were maintained at a constant temperature, approximately 24° throughout each experiment.

The two curves obtained by plotting the observed angle of rotation against time are shown in Fig. 1. It was not thought necessary to convert the observed rotation values to specific rotation values, since the solutions contained equal concentrations of glucose and had the same final volumes.

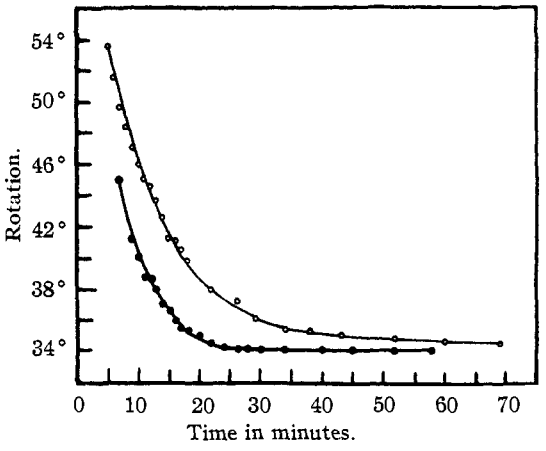

Fig. 1.—Polarimetric study of the glucose and glucose–$FeCl_3$ systems: ●, with $FeCl_3$; O, no $FeCl_3$.

The experiments were repeated using a freshly prepared sample of α-glucose. With the exception of an increase in the concentration of the ferric chloride solution to approximately 0.4 *M*, the conditions of the former experiments were reproduced. Data obtained in this case are shown in Fig. 2.

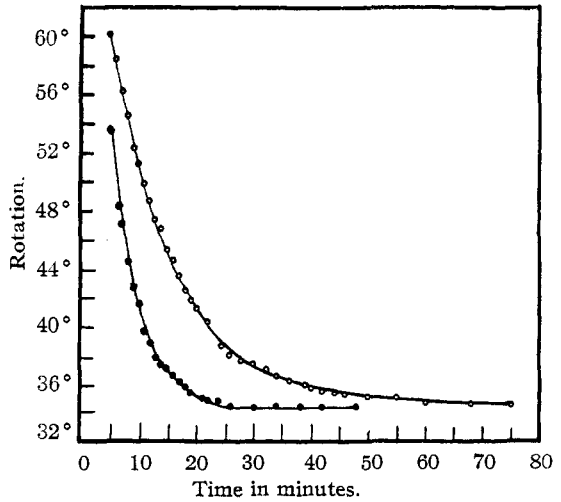

Fig. 2.—Polarimetric study of the glucose and glucose–$FeCl_3$ systems: ●, with $FeCl_3$; O, no $FeCl_3$.

The α-glucose used to obtain both curves of Fig. 1 differed in purity from that used to obtain both curves in Fig. 2. However, the two companion curves were obtained in each case with α-glucose of the same purity.

(1) An excerpt from a thesis submitted to the department of chemistry and the faculty of the graduate school of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Arts.

(2) NEPA Division, Fairchild Engine and Airplane Corporation, Oak Ridge, Tennessee.

(3) Hudson and Dale, THIS JOURNAL, **39**, 320 (1917).

Analysis of the Data.—The curves of Figs. 1 and 2 indicate that interaction occurs between the ferric chloride solution and the α-glucose solution, and that the presence of the ferric chloride increases the rate of mutarotation of the α-glucose. Our initial experiments, involving spectrophotometric studies of solutions of glucose and ferric ion in equilibrium, and utilizing the limiting logarithm method described by Bent and French[4] and the method of continuous variations as modified by Vosburgh and Cooper,[5] indicated the formation of at least one complex containing iron and glucose in equimolar amounts.

Since the conditions under which data for Figs. 1 and 2 were obtained were the same (with the exception of the variation in the concentration of the ferric chloride solution), only Fig. 2 will be considered in the following discussion. The upper curve of Fig. 2 shows the rate of mutarotation of the α-glucose in 0.1 *M* hydrochloric acid with no ferric chloride added. The first value shown, obtained five minutes after solid α-glucose was added to the hydrochloric acid, was 60.2°. As the curve indicates, no appreciable change in the rotation was observed after a period of approximately sixty minutes. The lower curve in Fig. 2 shows the rate of mutarotation of α-glucose in 0.1 *M* hydrochloric acid in the presence of 0.4 *M* ferric chloride. Again, the initial reading was made five minutes after the solid α-glucose was added to the solution. This reading (53.50) is appreciably lower than the previous reading. This curve levels off much more rapidly than the other, the observed rotation becoming constant after a period of approximately twenty-five minutes.

In any complex with iron(III) and glucose one might expect the ferric ion to be attached to the glucose molecule through the carbonyl oxygen. There is no reason to assume that this complexing should destroy the optical activity of the glucose molecule. It is known that an equilibrium exists between the α- and β-forms of glucose in solution. If the ferric ion were to combine with the α-form of glucose, one would expect the rate of mutarotation to decrease. Conversely, if the ferric ion were to combine with the β-form, the rate should increase. Since, in the case cited, the addition of the ferric ion results in an increased rate of mutarotation, it is concluded that the ferric ion complexes with the β- rather than the α-form of glucose.

This conclusion is supported by the slightly lower equilibrium optical rotation of the solution containing the ferric chloride. The difference between the two equilibrium values is of the order of the experimental error; however, approximately the same difference is noted for both series of runs. If the complex were formed with the α-rather than the β-form of glucose, one would expect the measured (*i. e.*, total) rotation at equilibrium to be greater than that for pure glucose solutions, which is precisely the opposite of the observed effect. Thus, assuming that the formation of the complex does not destroy the optical activity of the glucose molecule, one may say that the iron complexes preferably with the β-form.

(4) Bent and French, THIS JOURNAL, **63**, 568 (1941).
(5) Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

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Calculation of Resonance Energies

BY J. L. FRANKLIN

It has been shown that the heat of formation and free energy of formation of organic molecules are additive functions of characteristic group equivalents.[1,2] Since resonance energy is calculated as the difference between the heat of formation of a molecule and that of the corresponding structure assuming no resonance, it follows that the method of group equivalents can be used to calculate resonance energies. Further, this method automatically allows for steric effects and hyperconjugation.

Resonance affects electronic levels primarily and rotational and vibrational levels secondarily. Assuming no low-lying excited electronic levels, the electronic partition function is simply $e^{-E/RT}$ and the electronic entropy is zero. Consequently, a change in electronic energy due to resonance will have no effect on entropy. The rotational and vibrational entropy of a resonating molecule will be different from that of the corresponding hypothetical non-resonating molecule because of changes in bond distance, symmetry, and force constants. These might be expected to decrease slightly the entropy of the resonating molecule. It is observed, however, that resonance energies calculated from heats of formation and from free energies of formation are almost identical and vary but little with temperature so it might be concluded that the latter effects are small. Consequently, resonance energies may be calculated by the method of group equivalents from

TABLE I

CALCULATION OF RESONANCE ENERGY OF BENZENE

	ΔH_f^0	ΔF_f^0
$\begin{matrix}H\\H\end{matrix}\!\!>\!C\!=\!C\!<\!\begin{matrix}H\\H\end{matrix}$ (*cis*)	56.6	71.8
C_6 ring correction	−0.5	−6.4
Symmetry correction ($RT \ln \sigma$)	...	1.5
ΔH_f^0 or ΔF_f^0 for non-resonating structure	56.1	66.9
ΔH_f^0 or ΔF_f^0 for C_6H_6 from API[3] tables	19.8	31.0
Resonance energy	36.3	35.9

(1) Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).
(2) Bremner and Thomas, *Trans. Faraday Soc.*, **44**, 338 (1948).
(3) Selected Values of Properties of the Hydrocarbons, API Project 44, National Bureau of Standards Circular C461, Nov., 1947.