ties are introduced. By solving exactly the secular equation in form (3) instead of (1), we obtain resonance and excitation energies independent of α without having to assume the β's and S's constant for all distances and for different atoms. Each S is calculated using Slater functions. The parameters ρ_r, η, and $\beta_{1.33}$ (see (24) of ref. 1) are determined, as before, to fit experimental data. The variation of ρ with distance now found is less than half as rapid as before; $-\beta_{1.33}$ is increased from 44.5 to about 56 kcal.; and η is reduced from 4 to about 1.9.[3]

The improvement in our computations has been obtained without sacrificing essential simplicity and ease of computation; the results support the general validity of the molecular orbital approximation.

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[3] In sec. 14, we indicated that 4 is a reasonable value for η. Actually the present value is much more reasonable, since corrections previously neglected (cf. footnote 30) reduce the estimated η to about 1.5.

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CHICAGO, ILLINOIS CAROL A. RIEKE

RECEIVED APRIL 12, 1941

THE ACTION OF METHYLAMINE WITH NITROUS ACID

Sir:

In view of the experience of one of us (L. U. S.) in the successful quantitative determination of methylamine by the evolution of nitrogen on treatment with nitrous acid [Van Slyke, *J. Biol. Chem.*, **9,** 185 (1911)] it seems strange that methylamine should differ so greatly from *n*-butylamine in its reactivity with nitrous acid in aqueous hydrochloric acid solution [Whitmore, *et al.*, THIS JOURNAL, **54,** 3441 (1932); **63,** 1118 (1941)]. Apparently, the difference is due to the difference between an aqueous hydrochloric acid solution and an acetic acid solution containing no mineral acid and relatively little water. We now find that a solution of 1 mole of methylamine in 1 liter of glacial acetic acid when added to 5 moles of powdered sodium nitrite gives no appreciable action. On addition of 100 ml. of water, reaction starts and continues until about half a mole of nitrogen has been evolved. The reaction then slackens. An additional 100 ml. of water starts the reaction and finally gives, on heating, nearly half a mole of nitrogen. The gases were passed through dry-ice traps and a scrubber containing alkaline potassium permanganate. The chief organic product of the reaction was methyl acetate. The only other product isolated was a trace of methyl nitrite.

Apparently, the excess of nitrous acid and the minimum amount of water cut down the hydrolysis of methylamine nitrite earlier observed. It is also probable that the acetate ion with its cloud of electrons can make a more effective attack on the side of the carbon opposite the nitrogen than can hydroxyl ions, water molecules or chloride ions.

This work is being continued.

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STATE COLLEGE, PENNSYLVANIA FRANK C. WHITMORE
J. D. SURMATIS

RECEIVED MAY 6, 1941

p-AMINOBENZOIC ACID AND TYROSINASE ACTIVITY

Sir:

Since *p*-aminobenzoic acid has been reported to have chromotrichial activity [*Science*, **93,** 164 (1941); *J. Biol. Chem.*, **138,** 441 (1941)], we investigated its influence on dopa reaction and noted [*Proc. Soc. Exp. Biol. Med.*, **47,** May (1941)] it to modify enzymatic formation of melanin. Using the Warburg apparatus [kindly placed at our disposal by Reverend J. B. Meunzen, F.G., at Fordham University], we determined its effect on the kinetics of tyrosinase action. In numerous experiments, the detailed data of which are about to be published, we found that the aerobic oxidation of tyrosine and that of dopa is retarded by *p*-aminobenzoic acid, but that of *p*-cresol is accelerated. Qualitatively, aniline has the same influence as *p*-aminobenzoic acid; quantitatively, the effect of the latter is greater than that of the former.

In a typical set of experiments a reaction mixture was employed consisting of 0.4 ml. of 0.0463 M *p*-cresol, 1 ml. of McIlvaine buffer (*p*H 6.5), 0.5 ml. (2.5 mg.) of gelatin solution, 1 ml. of appropriately diluted enzyme solution [kindly furnished by Dr. J. M. Nelson, Columbia University; isolated from *psalliota campestris* and containing approximately 200 hydroquinone-catechol units and 50 cresolate units per ml. measured at 25°], and 1.1 ml. of water or 0.1 ml. of water and 1.0 ml. of 0.01 M solution of the test substance. All the determinations were made at a temperature of 37.2°, the rates of oxygen uptake were calcu-