

The Molecular Formula of Cephalosporin P₁

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THE chemistry of the steroidal antibiotic cephalosporin P₁ has so far been discussed¹ in terms of a molecular formula C₃₂H₄₈O₈ and a parent skeleton of 28 carbon atoms, the molecular weight having been determined by the X-ray crystallographic method. Recently a C₂₉ carbon skeleton has been proposed² for fusidic acid, a similar steroidal antibiotic. The molecular formula of cephalosporin P₁ has now been found to be C₃₃H₅₀O₈, the molecular weight having been kindly determined for us in

the laboratory of Professor C. Djerassi at Stamford University by mass-spectrometric examination of cephalosporin P₁ methyl ester and dideacetylcephalosporin P₁ lactone, using an improved injection technique. The parent skeleton has therefore 29 carbon atoms and an additional methyl group is presumably present, probably at position 8 of the basic steroid ring system. The implications of this closer relationship of cephalosporin P₁ to fusidic acid are being examined.

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¹ Burton, Abraham, and Cardwell, *Biochem. J.*, 1956, **62**, 171; Baird, Halsall, Jones, and Lowe, *Proc. Chem. Soc.*, 1961, 257.

² Godtfredsen and Vangedal, *Tetrahedron*, 1962, **18**, 1029.

A Kinetic Measurement for Fast Cation-Cation Oxidations in Solution

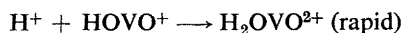
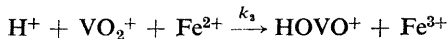
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THE use of rotating platinum electrodes in polarography, hitherto confined to oxidations involving only one ionic reactant,¹ can be extended to kinetic investigation of fast calomel-cation oxidations provided there exists a suitable applied voltage at which only one species gives a diffusion current. Thus if such an electrode in the system Fe^{II} + V^v $\xrightarrow{k_1}$ Fe^{III} + V^{IV} (in m-perchlorate), is connected by perchlorate solution as a bridge to a standard calomel electrode, and if a potential of 1.0v is applied across the cell, then a diffusion current i_d passes that is proportional only to the iron(II) concentration. Tests for electrode catalysis were negative. From second-order plots based on pen-recorder traces of the diffusion current against time, the rate constant k_1 showed an approximately 1.08th-power dependence on the (excess) hydrogen-ion concentration, indicating the following mechanism:



(Protonation of VO₂⁺ may actually occur in a pre-equilibrium; the non-integral 1.08th order arises from marginal participation of diprotonated VO₃⁺

or from an inconstancy of activity coefficients with medium changes²). The rate constant k_2 is 1.15 × 10⁵ l. mole⁻¹ sec.⁻¹ at 0°, E_a being 3.60 kcal./mole and $\Delta S_{25}^* = -33$ e.u. These values are consistent with the view that predominantly electrostatic effects accompanying the accumulation of charge.

Further reactions apparently amenable to this technique are the interactions Mn^{III}-V^{IV}, Mn^{III}-Fe^{II}, and Co^{III}-Fe^{II}.³ The rate constant of the last reaction does not conform with the Marcus equation,⁴ $k_{ox} = (k'k''K)^{\frac{1}{2}}$, k_{ox} (calc.)⁵ being 5 × 10⁹, and k_{ox} (obs.)³ being 23 l. mole⁻¹ sec.⁻¹. Conformance is expected because of close simulation by such transition-ion oxidations of the corresponding electron-exchange reactions (k' and k''), but it requires also a low equilibrium constant K . More favourable test reactions are V^{III}-Cr^{II} and Co^{III}-Mn^{II}, where k_{ox} (calc.)⁵ are 3 × 10⁻² and 3 × 10³ l. mole⁻¹ sec.⁻¹, respectively.

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¹ Kolthoff and Reynolds, *Discuss. Faraday Soc.*, 1954, **17**, 167.

² Higginson and Sykes, *J.*, 1962, 2841.

³ Bennett and Sheppard, *J. Phys. Chem.*, 1962, **66**, 1275.

⁴ Marcus, *Discuss. Faraday Soc.*, 1960, **29**, 21.

⁵ Bonner and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 3826; table III; Stranks, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 163; Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1952.