from progesterone and androstenedione [Marker, THIS JOURNAL, in press (1938)]. The details of this work will be published in a forthcoming issue of THIS JOURNAL.

We wish to thank Dr. Oliver Kamm and Parke, Davis and Company for their generous help and assistance in various phases of this work.

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RECEIVED MAY 21, 1938

KINETICS OF THE EXPLOSIVE REACTION BETWEEN HYDROGEN AND OXYGEN SENSITIZED BY NITROGEN PEROXIDE

Sir:

In a recent paper, von Elbe and Lewis [THIS JOURNAL, **59,** 2022 (1937)] propose a scheme of reactions for the above process, having concluded that "the evidence rules out a mechanism based on oxygen atoms." In arriving at this conclusion these authors did not discuss the relevant work of Norrish and Griffiths [*Proc. Roy. Soc.* (London), **A139,** 147 (1933)], and of Foord and Norrish [*ibid.*, **A152,** 196 (1935)] in which new evidence based on the study of the induction period and the effect of irradiation by light is presented.

Without dogmatizing about the precise nature of the chain mechanism we concluded in the light of the new facts that a mechanism involving oxygen atoms is by no means excluded. Such a scheme is indeed capable of giving a fair description of the facts and no other scheme has yet been advanced which has been shown to take our new facts into consideration.

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R. J. W. NORRISH

RECEIVED APRIL 20, 1938

EFFECT OF X-RAYS ON SURFACE POTENTIALS OF MULTILAYERS

Sir:

Porter and Wyman [THIS JOURNAL, **60,** 1083 (1938)] have reported that stearate X- or Y-films on grounded metal plates acquire negative potentials when exposed to x-rays.

We have produced charges on both X- and Y-multilayers in many different ways, measuring the potentials by the vibrating-plate method and with a polonium–air electrode. This work suggests that the ionized air and the electric field near the x-ray tube are responsible for the charge on the film.

We confirm Porter and Wyman's observation that a self-rectifying x-ray tube in air, operating on 60 kv., a. c., charges the films a few volts negatively even when either tube terminal is grounded. However, if an oil-immersed shockproof x-ray tube is used or if the metal plate is enclosed in a thin aluminum box, a 10-minute exposure, with the same x-ray dosage (28 roentgens), has no effect on the film potential.

Multilayer films exposed to x-rays from a tube in air, operated on 60 kv., d. c., acquire large potentials (10 volts on only 21 layers). The film becomes positively charged if it is at cathode potential and negatively charged if at anode potential, regardless of which terminal is grounded.

When there are high voltage terminals in air, the ionization of the air by x-rays permits a current to flow which can charge the film. We have found that with 60 kv., a. c., applied to a tube in air with its cathode cold so that no x-rays are generated, the films do not become charged. If, however, a pointed wire is attached to the anode terminal so that a corona discharge occurs, the plate becomes negatively charged although there are no x-rays.

A charged film on a grounded plate can be discharged in a few minutes if a grounded polonium electrode is brought close to its surface. Undoubtedly x-rays would discharge a charged film in an aluminum box if x-ray dosages of more than 100 roentgen units were used.

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RECEIVED MAY 24, 1938

THE RELATION BETWEEN RATES OF GENERAL BASIC CATALYSIS IN DIFFERENT REACTIONS

Sir:

It is a well-known characteristic of reactions which are susceptible to general catalysis by bases in the Brönsted sense that the logarithmic plot of catalytic constants k_B against corresponding basic association constants K_B yields several straight lines corresponding to the various charge types, rather than one single straight line.[1] Furthermore, certain substitutions on or near the re-

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[1] Kilpatrick and Kilpatrick, *Chem. Rev.*, **10,** 213 (1932); Pedersen, *J. Phys. Chem.*, **38,** 581 (1934).

acting center of the base also cause deviations even within a series of the same charge type.[3]

In view of these facts, extreme interest attaches to the accompanying figure, in which catalytic constants[4,7] for the mutarotation of glucose at 18° are plotted logarithmically against the corresponding catalytic constants[2,3,5,6] for the decomposition of nitramide at 15°, both in aqueous solution. The figure includes all the bases whose behavior in both reactions has been studied. No statistical corrections are made. The straight line has a slope of 2.00.

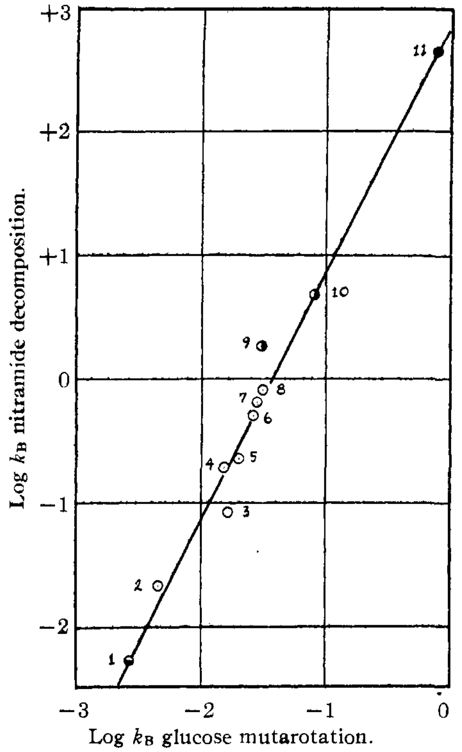

Fig. 1.—Plot of log k_B for nitramide decomposition against log k_B for glucose mutarotation: 1, betaine[2,7]; 2, salicylate[6,4]; 3, formate[3,4]; 4, benzoate[3,4]; 5, phenylacetate[3,4]; 6, acetate[3,4]; 7, propionate[3,4]; 8, trimethylacetate[6,4]; 9, quinoline[2,7]; 10, pyridine[2,4]; 11, $Co(NH_3)_5OH^{++}$[5,4].

It is immediately apparent that all the points fall reasonably well on the same straight line and that betaine, pyridine, quinoline and even $Co(NH_3)_5OH^{++}$ follow the same relationship which holds for the negative bases such as acetate ion. This is particularly startling in the case of $Co(NH_3)_5OH^{++}$, which in the familiar k_B *vs.* K_B plot deviates from the carboxylate ion curve by as much as two logarithmic units.

It is therefore highly desirable that knowledge of these and other reactions susceptible to general base catalysis be extended to include more bases in common. If the uniqueness of Fig. 1 is upheld by further extension of the data, it implies that the relationship between two series of rate constants for association by bases of protons from two different substrates is more fundamental than the relationship of either series of rate constants to corresponding equilibrium constants. It follows further that deviations which occur in the k_B *vs.* K_B relationships must originate in deviations in the relationships between the rate constants for association and dissociation; this also can be submitted to experimental study.

In its amenability to experimental attack, such an empirical approach differs from the theoretical approach embodied in the transition-state method which assumes the fundamental relationship to be between equilibrium constants and then attempts to derive the connection between rate and equilibrium constants by postulating an equilibrium between initial and transition states, the constant for which can unfortunately not be measured.[8]

SLATERSVILLE, R. I. HELMUTH L. PFLUGER

RECEIVED APRIL 25, 1938

INFLUENCE OF NICOTINIC ACID ON THE FERMENTATION METHOD FOR VITAMIN B_1 DETERMINATION

Sir:

Lohmann and Schuster[1] have shown that a vitamin B_1 pyrophosphate is identical with cocarboxylase. This coenzyme plays an essential part in the series of reactions which produce alcoholic fermentation and, in all probability, was present in the original Harden and Young extracts of cozymase. With regard to our fermentation method for vitamin B_1 determination,[2] it has been our working hypothesis that vitamin B_1, or the aminopyrimidine, is taken inside the

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[2] Work to be published by the writer.

[3] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[4] Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

[5] Brönsted and Volqvartz, *Z. physik. Chem.*, **A155**, 211 (1931).

[6] Baughan and Bell, *Proc. Roy. Soc.* (London), **158A**, 464 (1937).

[7] Westheimer, *J. Org. Chem.*, **2**, 431 (1937).

[8] See symposium in *Trans. Faraday Soc.*, **34**, 29ff. (1938).

[1] K. Lohmann and Ph. Schuster, *Biochem. Z.*, **294**, 188 (1937).

[2] A. S. Schultz, L. Atkin and C. N. Frey, THIS JOURNAL, **59**, (a) 948, (b) 2457 (1937).