## Structure of Urea

CONSIDERABLE evidence[1] has been presented for the polar structures I and II as important contributory forms of urea in aqueous solution and in the solid state. This view has been criticized by Bell, Gillespie and Taylor[2] on the grounds of electrometric titration data. The observation that buffering of urea solutions can only be detected at low pH values has been interpreted by these authors to mean that urea is a weak monacid base having the uncharged structure III. This result, however, would appear to be compatible with the polar structure of the molecule.

I   II   III   IV
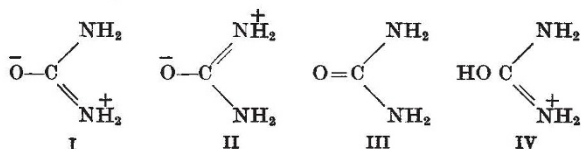
Either resonance structure I or II may be regarded as a substituted amidine in which the normal basic strength of this group has been considerably increased by the strong anionoidal characteristic of the attached O^- ($+ I$; $+ T$). This amidine ion would impart strong acid properties to the hydroxyl group of structure IV, of which urea may be regarded as the acid ion. The acid titration of urea may then be regarded as the back titration of a strong acid ($K > 10^{-1}$), and the alkaline titration as the back titration of a strongly basic substituted amidine, of such strength that buffering is absent in aqueous sodium hydroxide (cf. Bjerrum[3] on the titration data of amino-acids).

Volume of 1·449 $N/10$ sodium hydroxide (c.c.)
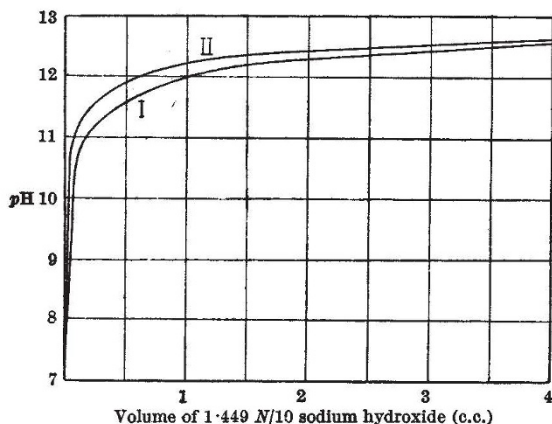
I, 10 c.c. $N/100$ BENZAMIDINE HYDROCHLORIDE ; II, 10 c.c. WATER

In support of this view the titration of benzamidine hydrochloride with sodium hydroxide (see graph), in which the O^- of urea may be regarded as having been replaced by the less anionoidal phenyl radical, shows slight buffering. The dissociation constant as computed from these data is of the order of $K_{20} = 10^{-2 \cdot 3}$.

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[1] For refs. see Taylor and Baker, "Organic Chemistry of Nitrogen", 280 et seq. (Oxford, 1937).
[2] Bell, Gillespie and Taylor, Trans. Farad. Soc., 39 137 (1943).
[3] Bjerrum, Z. phys. Chem., 104, 147 (1923).

Spread of Detonation in High Explosives

IN a recent communication[1], W. C. F. Shepherd makes the interesting observation that in the initial stages of detonation in a cylindrical cartridge of high explosive initiated with a detonator, a phase, referred to as the pre-detonation phase, is often noticeable during which the rate of propagation of the reaction is much lower than the stable value finally established. Moreover, "with progressively stronger initiators, the extent of the pre-detonation phase was correspondingly reduced and the rate of propagation during this phase was increased until, finally, there was no perceptible delay in the inception of detonation".

Having had occasion to study this phenomenon, we can confirm that, in certain high explosives, the detonation set up by a detonator may be of a lower order than that which eventually develops. In such cases, there is an initial unstable phase during which the reaction accelerates more or less rapidly until a point is reached at which the rate of detonation changes abruptly to a much higher value. This phenomenon is fairly common among liquid and gelatinous explosives and is illustrated in photographs Nos. 2, 7 and 10 of a previous paper by one of the present writers[2]. It is not generally known, however, that this effect can be produced in granular solid explosives like crystalline or granulated T.N.T. or tetryl, and that, under suitable conditions, such explosives exhibit the property, usually attributed only to liquid and gelatinous explosives, of being able to propagate detonation at two distinct velocities.
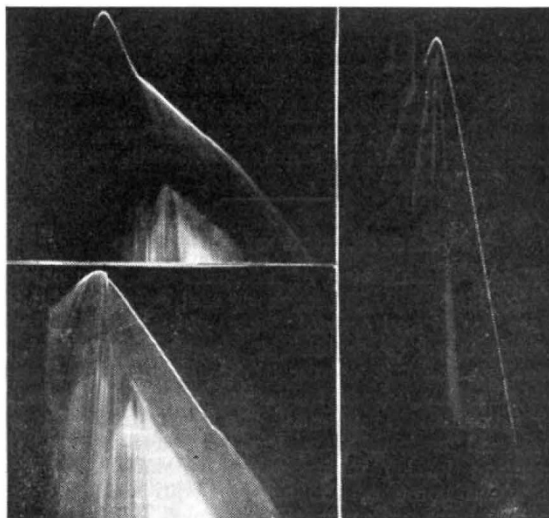
Fig. 1

Fig. 3   Fig. 2

The photograph reproduced in Fig. 1 illustrates the case where the initial regime is unstable and, after travelling a certain distance, changes abruptly to the higher detonation level. This record, which is almost identical with that of Shepherd, was obtained with a 1-in. diameter cartridge of granulated tetryl, size 20–30 B.S.S., cartridged at a density of 0·94 gm./c.c. and initiated with a No. 6 A.S.A. detonator. As Shepherd points out, the length of the