ϵ *ca.* 2.9 at 250 mμ, 4.2 at 210 mμ).[7] With pyridine–sulfur trioxide in pyridine overnight at room temperature, V furnished the tetraacetylglucotropaeolate ion VI, isolated as the monohydrated potassium salt, m.p. 186.5–187° dec. (lit.[8] 187–189° dec.), $[\alpha]^{32}D$ −22.6° (water), identified by infrared spectrum with specimens derived[8] from nature. The ion was also isolated, in 53% yield from V, as **tetramethylammonium tetraacetylglucotropaeolate,**[4] m.p. 182.5–183.5° (anhydrous form), $[\alpha]^{28}D$ −18.9° (water), converted in 94% yield by methanolic ammonia[8,9] to anhydrous **tetramethylammonium glucotropaeolate,**[4] the salt of I (R = $C_6H_5CH_2$), m.p. 188–189.2° dec., $[\alpha]^{28}D$ −16.7° (water). The glucotropaeolate was identical with a sample isolated from *Tropaeolum majus* seed by adsorption of an extract[8] on anion exchange resin and elution with tetramethylammonium hydroxide.[10] When the synthetic glucotropaeolate was treated with the usual protein fraction of yellow mustard, benzyl isothiocyanate (II, R = $C_6H_5CH_2$) was rapidly[11] formed in quantitative yield and was determined and isolated as benzylthiourea.

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(7) Ammonolysis of V afforded S-β-D-1-glucopyranosylphenylacetothiohydroximic acid, m.p. *ca.* 115° (hydrate), $[\alpha]^{28}D$ −44° (water), which was attacked by myrosin, if at all, with not more than one fiftieth of the rate of cleavage of the sulfated analog I (R = $C_6H_5CH_2$) and was not converted to benzyl isothiocyanate. The likelihood that rearrangement of I and departure of the sulfate and glucosyl groups are simultaneous renders dubious the accepted division of myrosin into thioglucosidase and sulfatase.

(8) O.-E. Schultz and W. Wagner, *Arch. Pharm.*, **288**, 525 (1955). Other monohydrated samples of natural or synthetic origin melted as low as 140–150° (dec.).

(9) A. Kjaer and R. Gmelin, *Acta Chem. Scand.*, **10**, 335 (1956).

(10) On isolation of amorphous potassium glucotropaeolate and hydrolysis to phenylacetic acid, see O.-E. Schultz and R. Gmelin, *Arch. Pharm.*, **287**, 342 (1954).

(11) The glucotropaeolate was cleaved to mustard oil approximately twice as fast as was natural glucosinalbate.

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RECEIVED FEBRUARY 8, 1957

RELAXATION PHENOMENA AND CONTACT ANGLE HYSTERESIS

Sir:

We wish to advance a kinetic mechanism for contact angle hysteresis as observed by Bartell and Bjorklund[1] on high energy smooth surfaces. Verwey[2] has presented evidence for the existence of an ice-like structure at the water–vacuum interface, and Grahame[3] has found evidence for a similar structure at the water–mercury interface. Recently Bockris, Mehl, Conway and Young[4] have proposed that water is oriented in an ice-like structure at the water–copper interface, and that its dielectric relaxation time there is about 10^{-6} sec. (as compared to 10^{-10} sec. for bulk water at room temperature).

These findings appear relevant to contact angle hysteresis on smooth surfaces. The measurement of a contact angle involves displacement of a periphery formed by the three-phase junction across one of the phases. There is a natural length associated with this process, namely, the peripheral thickness l. Just as the surface of discontinuity between two phases is not a mathematical surface, so the periphery is not a mathematical curve, but will have a thickness of the same order of magnitude as the surface of discontinuity. This latter thickness is normally taken as the distance over which concentration gradients are appreciable (at equilibrium), and is of the order of magnitude of molecular dimensions. A parallel definition of peripheral thickness can be made, and it should be of the same order of magnitude. There is a natural time associated with this process, namely, the relaxation time τ of the most slowly relaxing molecule at the periphery. There is therefore a natural displacement velocity $V_N = l/\tau$. Let V be the actual displacement velocity; then if $V << V_N$ the displacement should be quasistatic and all boundary tensions operating at the periphery should be equilibrium tensions, but if $V >> V_N$, then at least the most slowly relaxing molecule will be disoriented at the periphery, and boundary tensions at the periphery (which determine the contact angle) at interfaces involving this molecule will exceed their equilibrium values. On standing, the disoriented molecules will orient and the periphery will move, but at a velocity approximating V_N.

Now $l \sim 10^{-8}$ cm., and if we assume $\tau \sim 10^{-3}$ sec. it is possible to rationalize the experiment of Bartell and Bjorklund[1] involving substantial equality of contact angles formed by advanced and immediately (but slowly) receded water drops in the mercury–water–heptane system. Even more extreme time effects should be expected in systems such as water–heptane–silica, since adsorption at the water–silica boundary appears to involve formation of a surface silicic acid. If $\tau \sim 1$ sec. for this process, $V_N \sim 10^{-8}$ cm./sec. or about 0.01 mm./day. Most observers would consider such a drop motionless.

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CRYSTALLINE PHOSPHORUS PENTANITRIDE, P_3N_5

Sir:

Phosphorus nitrides generally are reported to be amorphous. In one exception,[1,2] a crystalline

(1) F. E. Bartell and C. W. Bjorklund, *J. Phys. Chem.*, **56**, 453 (1952).

(2) E. J. W. Verwey, *Rec. trav. chim.*, **61**, 564 (1942).

(3) D. C. Grahame, *J. Chem. Phys.*, **23**, 1725 (1955).

(4) J. O'M. Bockris, W. Mehl, B. E. Conway and L. Young, *ibid.*, **25**, 776 (1956).

(1) H. Moureu and P. Rocquet, *Bull. soc. chim.*, [5] **3**, 1801 (1936).

(2) H. Moureu and G. Wetroff, *ibid.*, [5] **4**, 918 (1937).

phase was thought, without proof of composition, to be $(PN)_n$. We have found that the crystalline phase produced under the conditions described, and under other conditions, is P_3N_5.

The solid phosphorus nitrides produced by use of electrical discharges are amorphous to X-rays and usually are heterogeneous in appearance. They decompose at 800 to 900° in a vacuum or in ammonia or nitrogen. The volatile products are mainly the elements; under suitable conditions, a homogeneous amorphous nitride with an N:P atomic ratio of unity can be condensed therefrom. The properties of the residual solid depend upon the starting material and its treatment.

Effects of several treatments on various amorphous nitrides are shown in Table I. The heterogeneous amorphous mixtures (products of arc synthesis) invariably yielded crystalline residues with the same X-ray pattern, and the intensity of the pattern increased as the N:P ratio approached 1.66. The conversion of amorphous to crystalline phase was accompanied by an expansion.

TABLE I

REACTIONS OF AMORPHOUS NITRIDES IN VACUUM, AMMONIA AND NITROGEN AT 800 TO 900°

Initial material (amorphous)		Residual product	
Appearance[a]	Atomic ratio N:P	Atomic ratio N:P	Crystallinity[b]
In vacuum, 10^{-3} to 10^{-4} mm.			
Homogeneous	0.98	0.98	Absent
	1.48	1.48	Absent
Heterogeneous	1.25	1.60	Strong
	1.25	1.65	Very strong
In ammonia, 1 atm.			
Homogeneous	0.99	1.62	Very weak
	1.48	1.58	Very weak
Heterogeneous	1.22	1.27	Very weak
	1.22	1.61	Weak
	1.22	1.63	Strong
	1.22	1.66	Very strong
In nitrogen, 1 atm.			
Homogeneous	0.99	1.46	Weak
	1.48	1.35	Absent
Heterogeneous	1.26	1.56	Medium

[a] Under microscope. [b] All crystalline phases gave same X-ray pattern.

Homogeneous amorphous materials with N:P ratios of 1 and 1.5—corresponding to $(PN)_n$ and $(P_2N_3)_n$—reacted similarly with ammonia to yield the same crystal phase. The mononitride also reacted with nitrogen. Neither of these materials, however, changed in N:P ratio or yielded a crystalline phase when heated in a vacuum.

It was concluded that the crystalline phase was P_3N_5. The interplanar spacings, d, and the relative intensities, I, are shown in Table II.

TABLE II

X-RAY POWDER DIFFRACTION PATTERN OF P_3N_5[a] (Cu K_α RADIATION[a]

d, Å.	I	d, Å.	I	d, Å.	I
4.56	S	2.02	MW	1.34	W
4.20	M	1.83	VW	1.29	W
3.60	VS	1.71	W	1.21	W
2.72	MW	1.61	W	1.20	W
2.55	VW	1.53	M	1.17	VW
2.43	MW	1.50	W	1.12	W
2.36	MW	1.46	MW	1.08	W
2.27	MW	1.41	W	1.04	VW

[a] Determined by James P. Smith.

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PHOSPHORYLATION COUPLED WITH PYRIDINE NUCLEOTIDE OXIDATION[1]

Sir:

We are reporting herewith mitochondrial phosphorylations in beef heart and honey bee thoracic preparations. These phosphorylations are coupled to oxidation of triphosphopyridine nucleotide (TPNH), and also depend upon an enzyme or enzymes present in the "soluble" fraction of the cells, *i.e.*, the portion not sedimented by centrifuging up to 105,000 × *g*.

Table I records the oxidation and phosphorylation observed when TPNH is the substrate. Results are similar with catalytic amounts of TPN in the glucose-6-PO_4 or 6-phosphogluconate oxidation systems. It is evident that the "soluble" fraction, which contains the pentose cycle complex,[2] does not possess the necessary terminal electron transport enzymes to promote TPNH and pentose cycle oxidations. On the other hand, both the "soluble" fraction and the mitochondria are required for oxidative phosphorylation, in contrast to Krebs cycle oxidations where the mitochondria alone can suffice. Freshly prepared sarcosomes from honey bee thoraces also oxidize TPNH with concomitant phosphorylation, but do not require a "soluble" fraction. The P/O ratios in the honey bee are low (0.2) both with TPNH and Krebs cycle intermediates because of an active ATPase in the preparations.

Against the possibility that the phosphorylations may have been due to glycolysis (from ADP-myokinase-glucose-hexokinase), additional experiments were carried out using glucose-C^{14} and inhibitors. By using glucose-1-C^{14} or glucose-6-C^{14} in the presence or absence of iodoacetate it was found that the phosphorylation associated with TPNH oxidation was not due to glycolysis. Similar P/O ratios were observed during oxidation of DPNH. This may be due at least in part to glycolysis.

The simultaneous requirement for both the "soluble" and particulate fraction to promote oxidative phosphorylation with TPNH is observed either with fresh or frozen and thawed preparations. While problems of mitochondrial permeability to TPN and TPNH remain to be settled,

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(2) R. W. Newburgh and V. H. Cheldelin, *ibid.*, **218**, 89 (1956).