

*Citation:*

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1 mm.), not even when the heating was continued for 48 hours.

On the contrary, the dilatometer having been kept at 15° during a month, the change was:

At 101°.8 in 2 hours, + 74 mm.; i.e. + 37 mm. per hour

„ 100.9 „ 1 1/3 „ + 20 „ ; „ + 15 „ „ „

„ 100.2 „ 12 „ - 89 „ ; „ - 7 1/2 „ „ „

From these data one might conclude that there exists a transition point in the neighbourhood of 101° which is in perfect agreement with our density determinations (§ 4—6).

10. Guided by the experience gained in the case of cadmium and copper <sup>1)</sup>, we now carried out some experiments with antimony whose previous thermal history had been changed between wide limits.

After having kept the dilatometer for 50 minutes at 150°, the meniscus fell during a certain time at the constant temperature of 96°.0; after this it became *stationary* and then began to *rise*. From these observations one would conclude that there is a transition point below 96°.0 and that, in consequence of the heating at 150°, the transition temperature had thus been lowered. This experiment proves, that at 96°.0 there are present at the same time more than two modifications.

11. The dilatometer was now kept at 225° for 12 hours. After this there occurred at 94°.6 (at constant temperature) a marked fall in the oil level (569 mm. within 48 hours), while in the experiment described in § 10 there took place a rise of the meniscus at the same temperature.

12. The phenomena described above show that *metallic* antimony, such as we have known it hitherto, is also a metastable system which consists of more than two allotropic forms.

We hope shortly to report on the modifications which play a rôle here.

Utrecht, April 1914.

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**Chemistry.** — “*The Coloration of some derivatives of Picrylmethylamide with alkalies*”. By Prof. A. P. N. FRANCHIMONT and H. J. BACKER.

(Communicated in the meeting of September 26, 1914).

In a previous communication (*Rec. trav. chim.* 1913, **32**, 325; *Abstr. Chem. Soc.* 1914, ii, 84) we described the spectrographic investigation of the coloration which picrylalkylnitramines undergo by alkalies. It was shown, that the absorption spectrum of picrylmethylnitramine  $C_6H_2(NO_2)_3NMe(NO_2)$  after addition of alkali gets a certain ana-

<sup>1)</sup> Proceedings **17**, 54, 60 (1914).

logy with that of picrylmethylamide  $C_6H_2(NO_2)_3NHMe$ , and that the latter spectrum is not much changed by alkali.

We then concluded, that the coloration of picrylalkylnitramines with alkalies had a similar cause as the colour of nitranilines (*vid.* FRANCHIMONT, *Rec. trav. chim.* 1910, **29**, 298, 313), which is ascribed by HANTZSCH (*Ber.* 1910, **43**, 1669) to an action between the nitro and amino groups attached to the benzene nucleus. The coloration of the nitramines would thus be produced by nitro groups of the nucleus reacting with the base, the nitro group attached to nitrogen playing only a secondary part.

In order to test this hypothesis, we have now examined several derivatives of picrylmethylamide, compounds of the formula  $Picr. NMeX^1)$ . For X we have chosen the nitroso group, the organic acyl groups  $COCH_3$ ,  $CO_2Me$ ,  $CO_2Et$  and finally the phenyl group as example of a negative group being no acylgroup. The compounds investigated were thus picrylmethylnitrosamine  $Picr. NMe(NO)$ , picrylmethylacetamide  $Picr. NMe(COCH_3)$ , methylpicrylmethylaminoformiate  $Picr. NMe(CO_2Me)$  and the ethylester  $Picr. NMe(CO_2Et)$ , and picrylphenylmethylamide  $Picr. NMePh$ .

In the first place it should be observed that, like the nitrogroup, also the acyl groups  $NO$ ,  $COCH_3$ ,  $CO_2Me$ ,  $CO_2Et$  strongly diminish the colour of the picrylmethylamide. Compared with this deeply yellow coloured amide, the nitramine, nitrosamine, acetyl derivative and both the urethanes are only palish yellow.

These differences are clearly shown by the absorption curves. Both the absorption bands of picrylmethylamide at  $\frac{1}{2}$  2390 and 2875 (see curve 15) disappear wholly; the acyl derivatives give for the concentrations examined, only a continuous absorption in the ultra-violet (curves 3, 5, 8, 10), just as it was found for the nitramine (*Rec. trav. chim.* 1913, **32**, 332).

It must be admitted, that the presence of acyl groups in the aminogroup of picrylmethylamide so strongly diminishes the basic properties of this group, that it loses the power to act with a nitrogroup, and thus to produce colour.

If this hypothesis is correct, it must be possible to prevent this reaction also by addition of a strong acid combining with the amine group.

Indeed, picrylmethylamide dissolves perfectly colourless in strong

<sup>1)</sup> In this paper *Picr.* means the group 2, 4, 6-trinitrophenyl.

sulphuric acid. The absorption bands disappear wholly from the spectrum, and only a modest continuous absorption in the ultraviolet remains (compare curves 14 and 15). For a concentration of 0.0002 gram-molecules per litre and an absorbing layer of 100 m.m. the beginning of the absorption is repelled by the sulphuric acid from  $\frac{1}{\lambda}$  2150 to 3400. This decoloration of picrylmethylamide by sulphuric acid is just the reverse of the coloration of the nitramine with alkali. In the first case the nitro groups of the nucleus are deprived of the opportunity to combine with a basic group, in the latter case this opportunity is on the contrary given.

The reaction with alkalies seems to be the same for the acyl derivatives now investigated as for the picrylalkylnitramines, the only difference being that they want a little more alkali for the red coloration. Formerly we found (*Rec. trav. chim.* 1913, **32**, 332), that a solution of picrylmethylnitramine containing an excess of alkali gives two bands at  $\frac{1}{\lambda}$  1975 and 2350. At nearly the same places two bands are shown by the alkaline solutions of the acetyl derivative (curve 6) and the urethanes (9 and 11), though one of the bands is only represented by a flat part of the absorption curve.

The anomalous curve given by the nitrosamine with alkali (4) will be discussed separately.

Picrylphenylmethyamide, the last derivative of picrylmethylamide we examined, exists in two forms of the same dark red colour but of different melting points, 108 and 129°. HANTZSCH (*Ber.* 1910, **93**, 1651) calls the two forms homochromo isomerides, whilst BILMANN (*Ber.* 1911, **44**, 827) regards them as polymorphous forms.

As HANTZSCH has already observed, the spectra of the two forms are completely equal (curve 12). It was now found, that the  $\alpha$  and  $\beta$  forms in presence of alkalies also behave in the same way (curve 13), so that the two forms when dissolved seem to be wholly identical. The broad absorption band of the amide at 2350 becomes by addition of alkali a little deeper and is somewhat displaced to larger wavelengths. At the same time it undergoes a division into a flat part at 2070 and a feeble band at 2400. This agrees with the behaviour of the other compounds with bases.

Finally we have examined the coloration of 1,3,5-trinitrobenzene with alkali, since here only the nitrogroups of the nucleus can act with the base.

Whilst trinitrobenzene only absorbs continuously (curve 1), addition

of alkali produces a broad band from 2040 to 2300 (curve 2). Its centre is at about the same place as the centre of the two bands, which show the picrylmethylamide derivatives in presence of alkalies.

In the previous publication (l.c.) we mentioned a remarkable decomposition of the alkaline solution of picrylmethylnitramine. After a day it gave the spectrum of potassium picrate, being hydrolysed in this way :  $\text{Pier. N Me NO}_2 \rightarrow \text{Pier. OH} + \text{Me NH NO}_2$ .

An analogous decomposition takes place, though more slowly, with the acetyl derivative and the two urethanes. In a few days the spectrum of their alkaline solutions is perfectly the same as that shown by potassium picrate (curve 7).

With picrylmethylnitrosamine this decomposition proceeds very quickly, much more rapidly than with the nitramine. During the few minutes required for the spectrographic examination its alkaline solution is already partly decomposed.

The anomalous absorption curve (4) is apparently due to a superposition of the spectrum of the potassium compound of the nitrosamine with that of potassium picrate. From the three bands shown by this curve at  $\frac{1}{\lambda}$  2000, 2400 and 2900 the latter is undoubtedly caused by the presence of potassium picrate, which gives a band at about 2880. In the spectrum of the potassium compound of the nitrosamine there may be expected two bands at about 2000 and 2350, in analogy to the observations made with the other derivatives of picrylmethylamide. The former band is indeed present, whilst the second band, likely with assistance of the flat band shown by potassium picrate at 2500, is transferred to 2400. Two hours after its preparation, the alkaline solution of the nitrosamine was again examined; it then showed the pure spectrum of potassium picrate (curve 7).

The results of this investigation may be expressed as follows.

The coloration of picrylmethylnitramine by alkali has the same cause as the coloration of other derivatives of picrylmethylamide by this reagent.

For the nitramine, the acetyl-, carboxymethyl- and carboxyethyl-derivatives, which altogether only have continuous absorption for ultraviolet rays, show two bands at about 2000 and 2350 after addition of alkali. Picrylphenylmethylamide has already of itself an absorption band, which, however, by alkali is divided into two parts at 2070 and 2400.

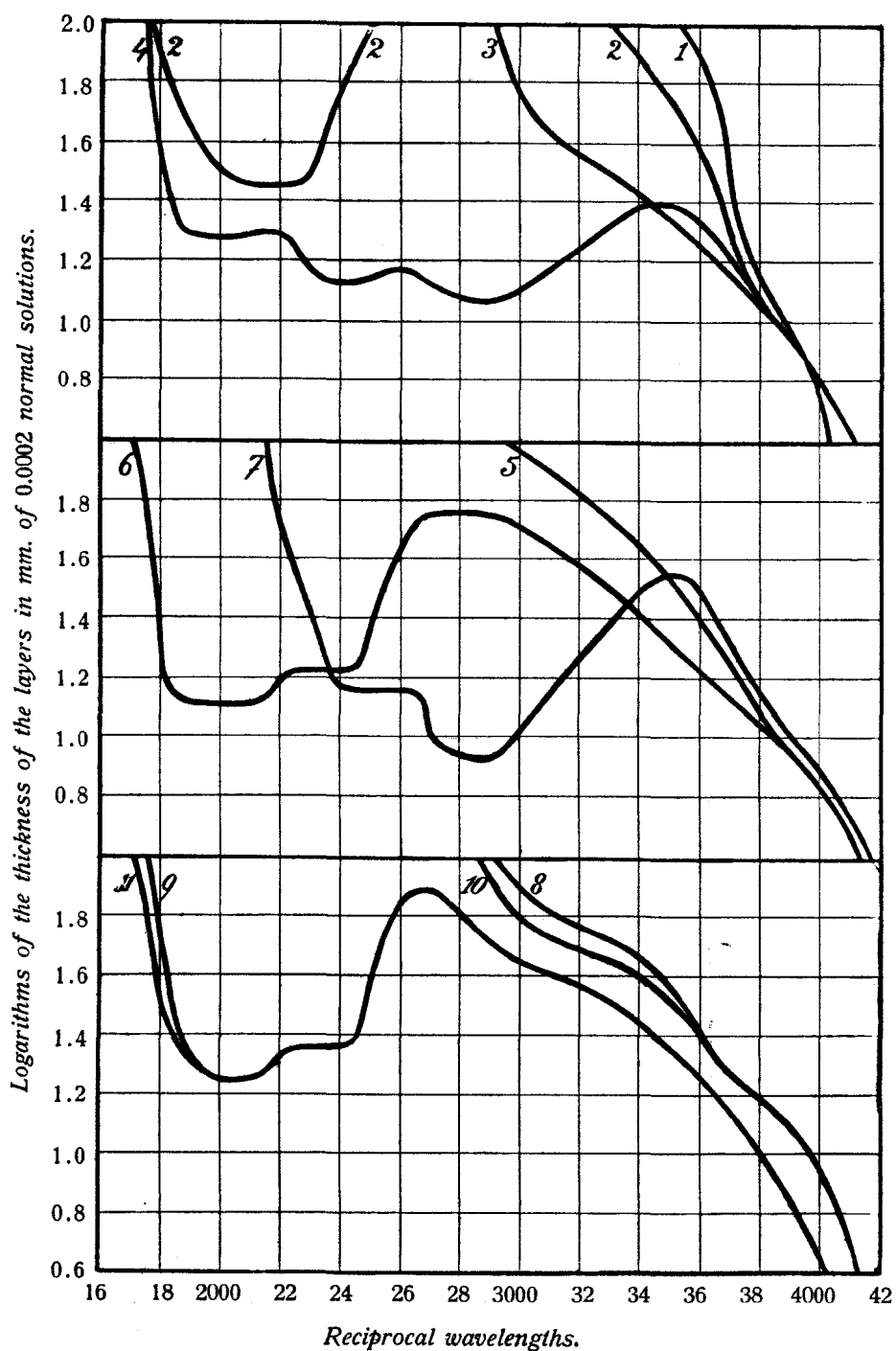


Fig. I. 1. 1,3,5-Trinitrobenzene. 2. id. + KOH. 3. Picrylmethylnitrosamine. 4. id. + KOH. 5. Picrylmethylacetamide. 6. id. + KOH. 7. Picric acid + KOH. 8. Methyl picrylmethylaminoformiate. 9. id. + KOH. 10. Ethyl picrylmethylaminoformiate. 11. id. + KOH.

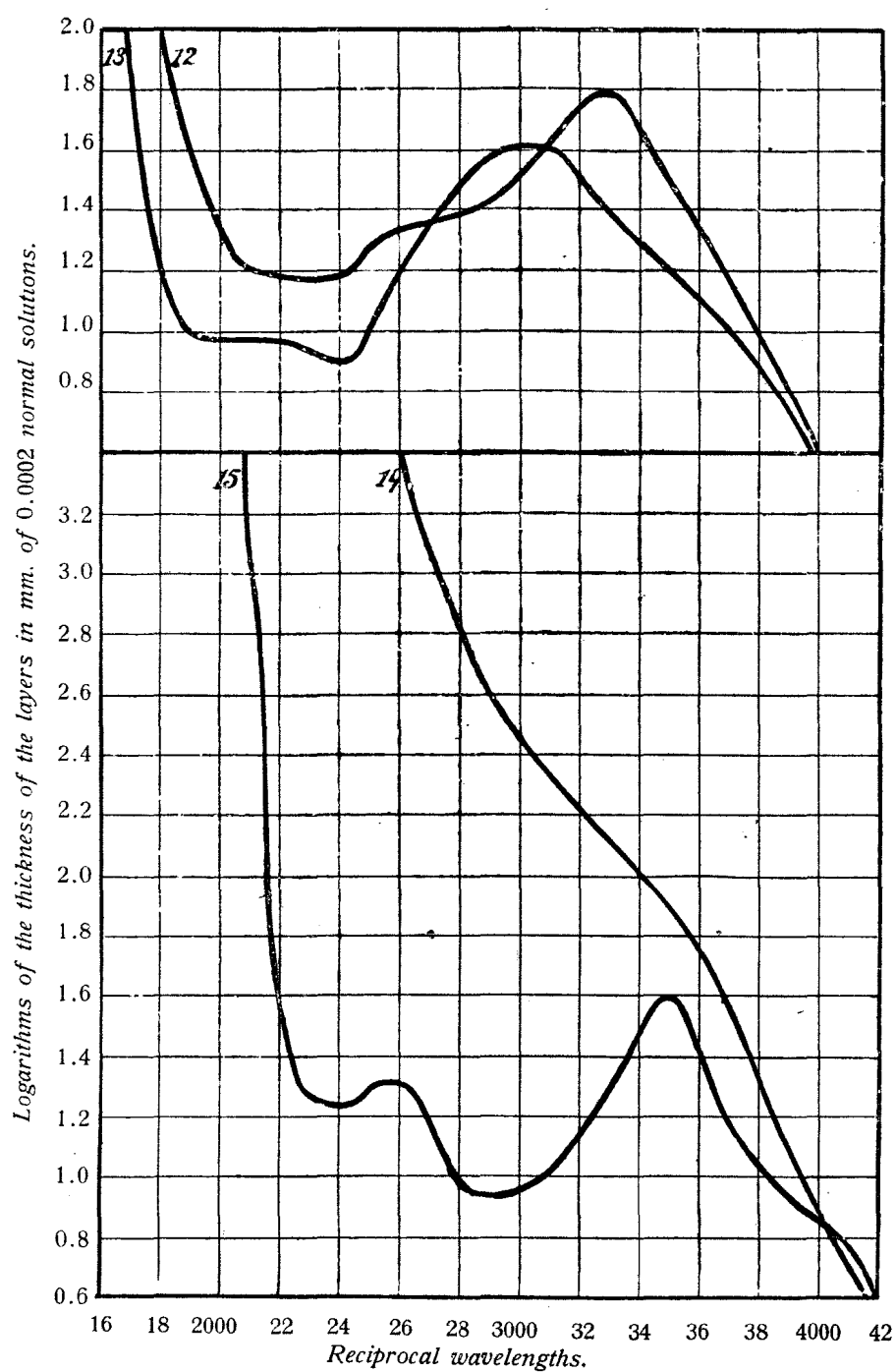


Fig. II. 12. Picrylphenylmethanamide ( $\alpha$  &  $\beta$ ). 13. id. + KOH. 14. Picrylmethanamide in sulphuric acid. 15. Picrylmethanamide.

The nitrogroup attached to the nitrogen atom of the nitramine is evidently not essential for the reaction.

Further, the spectrum of trinitrobenzene with alkali, though much differing from that of the other alkaline solutions, has yet its absorption in about the same part  $\left(\frac{1}{\lambda} \text{ 1800—2500}\right)$ .

We may thus conclude, that in all these cases the coloration is produced by a reaction of the base with one or more nitrogroups of the nucleus.

Finally it has been shown, that the presence of a strong acid, as well as the introduction of acyl radicals, completely expels the absorption bands of picrylmethylamide.

**Chemistry.** — " *$\alpha$ -Sulpho-propionic acid and its resolution into optically active isomerides*". By Prof. A. P. N. FRANCHIMONT and Dr. H. J. BACKER.

(Communicated in the meeting of September 26, 1914).

Already in 1902 a great number of diverse chemical and biochemical methods were tried by the first of us to separate the  $\alpha$ -sulphopropionic acid  $\text{CH}_3(\text{SO}_3\text{H})\text{CHCO}_2\text{H}$  prepared by him <sup>1)</sup> from propionic anhydride and sulphuric acid, into the two optical isomerides that one might expect according to theory. Not a single one, however, had given the desired result, although sometimes strychnine salts with a different rotating power were obtained, but after their conversion into ammonium salts these always appeared to be inactive.

As SWARTS <sup>2)</sup> had stated that he certainly had obtained from fluorochlorobromoacetic acid strychnine salts with varying rotating power, but had not succeeded in isolating the optically active acids. and as also PONCHER <sup>3)</sup>, who tried to effect a separation of bromochloromethanesulphonic acid by means of cinchonine, only obtained rotating ammonium and barium salts, but no acids, it appeared as if with such simple acids the tendency to form racemic mixtures or compounds was very great and likewise the velocity of conversion. This was provisionally also assumed in the case of  $\alpha$ -sulphopropionic acid (methylsulphoacetic acid) and the experiments were discontinued in consequence.

Still with lactic acid (methyloxyacetic acid) PURDIE and WALKER <sup>4)</sup>

<sup>1)</sup> Rec. d. Tr. ch. d. P.B. 7. p. 27 (1888).

<sup>2)</sup> Bull. Ac. Belg. (3) 31. p. 25 (1896).

<sup>3)</sup> Bull. Soc. ch. (3) 27. p. 438 (1903).

<sup>4)</sup> J. ch. Soc. 61. p. 754 (1892).