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Technical note

Unusual induction in the iodine–azide induced reaction exhibited by organophosphorus compounds on thin-layer chromatography plates

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Abstract

A comparative investigation of the TLC detection systems for the class identification of tri- and pentavalent organophosphorus compounds was carried out. The results show for the first time that the iodine–azide reaction can also be induced by organophosphorus compounds lacking a sulphur atom. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The induced iodine–azide reaction, originally carried out by Raschig [1], has been explored for decades in analytical chemistry [2–6]. As the result, hundreds of papers have been published in the literature, describing the application of the induction activity of this reaction, represented schematically in Eq. (1), exhibited a number of compounds that contain divalent sulphur.



However, until now, there has not been a report in the chemical literature describing the induction of the

iodine–azide reaction caused by compounds which do not contain a sulphur atom in the molecule of an inductor.

Recently we have published a report on the induction activity of thiophosphoryl compounds (P–S inductors) in the iodine–azide reaction, and its analytical applications in area of quantitative determination [7,9] and TLC detection [8,10,11] of these compounds.

When we started supplementary research on the scope and the limitations of the application of the iodine–azide reagent in the chemistry of organophosphorus compounds, we have revealed a very unusual phenomenon.

In this paper we would like to present our results on the TLC detection of the selected group of tri- and pentavalent organophosphorus derivatives,

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Table 1

Comparison of the TLC detection limits (μg per spot) of phosphorus compounds by means of UV (254 nm), the iodine–azide reagent and other representative detection reagents

Compound applied		UV	$\text{I}_2\text{-N}_3^-$ ^c	I_2 ^e	DDQ ^f	Mn ^h	Nin ^j	Mo ⁿ	R_F
No.	Structure ^a	μg	μg	μg	μg	μg	μg	μg	
1a	(MeO) ₂ P(O)H	–	3	10	3	3	10	–	0.48 ^p
1b	(EtO) ₂ P(O)H	–	10	10	3	3	10	–	0.55 ^p
		–	15						0.72 ^r
		–	3						0.63 ^s
1c	(iPrO) ₂ P(O)H	–	10 ^{d,e}	10	3	3	10	–	0.60 ^p
1d	(BuO) ₂ P(O)H	–	3	10	3	3	10	–	0.65 ^p
1e	(PhO) ₂ P(O)H	10	10	10	3 ^o	3	10	–	0.70 ^p
			3						0.70 ^r
			30						0.70 ^s
2a	(MeO) ₃ P	–	3	10	3	3	10	–	0.50 ^p
2b	(EtO) ₃ P	–	3	10	3	3	10	–	0.55 ^p
			10						0.72 ^r
			3						0.63 ^s
2c	(iPrO) ₃ P	–	30 ^{d,e}	10	3	10	10	–	0.61 ^p
2d	(BuO) ₃ P	–	10 ^{d,e}	10	3	10	10	–	0.64 ^p
2e	(PhO) ₃ P	10	3	10	3 ^o	3	1 ^k	30	0.72 ^p
			1						0.81 ^r
			3						0.00 ^s
3	Hex ₂ P(O)H		2 ^e	10	30 ^g	2	10	–	0.45 ^p
4	Ph ₂ (EtO)P	10	10 ^e	10	3 ^o	3	3	–	0.51 ^p
5a	Ph ₃ P	1	3	1	3	3	1 ^k	3	0.71 ^p
			10 ^e						0.73 ^r
			10 ^e						0.00 ^s
6a	(EtO) ₃ P=O	–	10 ^e	10	–	–	–	–	0.53 ^p
6b	(PhO) ₃ P=O	3	3 ^e	10	–	–	–	–	0.68 ^p
7	NaH ₂ PO ₂	–	30 ^{d,e}	10	–	1	30	10	0.36 ^t
8	H ₃ PO ₃	–	3 ^{d,e}	10	–	1 ⁱ	20 ^l	10	0.66 ^t
9	Et–P(O)(OH) ₂	–	–	–	–	1 ⁱ	20 ^l	1	0.72 ^t
10	Et–CH–P(O)(OH) ₂	–	–	–	–	1 ⁱ	20 ^l	10	0.64 ^t
	OH								
11a	Et–CH–P(O)(OH) ₂	–	–	–	10 ^g	1 ⁱ	–	0.2	0.30 ^t
							0.1 ^m		0.22 ^w
	NH ₂								
11b	Met–CH–P(O)(OH) ₂	–	–	–	10 ^g	1	–	1	0.45 ^t
							0.1 ^m		0.22 ^w
	NH ₂								
12	H ₃ PO ₄	–	–	–	–	1 ⁱ	10 ^l	0.2	0.51 ^t
13	(EtO) ₂ P(O)OH	–	–	–	30	3 ⁱ	20 ^l	1	0.80 ^t
14	(PhO) ₂ P(O)OH	10	–	–	30	3 ⁱ	–	1	0.80 ^t

^a Bu = *n*-butyl; Et = ethyl; Hex = *n*-hexyl; iPr = isopropyl; Me = methyl; Ph = phenyl; Met = methylthioethyl. ^b “–” = not detectable at 50 μg per spot. ^c White spots on a yellow background. ^d Appeared after 15 min. ^e Brown spots. ^f Navy-blue spots on a grey–green background after exposition in ammonia vapour. ^g Pink spots after exposition in ammonia vapour. ^h Light green–grey spots on a light-brownish background. ⁱ Pink spots on a light-brownish background. ^j Pink spots after preheating to ca. 100°C. ^k Pink spots without heating. ^l White spots on a faint-pink background. ^m Blue spots after preheating to ca. 100°C. ⁿ Blue spots after irradiation at 360 nm. ^o Red spots without ammonia vapour. ^p TLC system: silica gel–acetone. ^r TLC system: alumina oxide–acetone. ^s TLC system: reversed-phase plates (RP-18)/acetone–water (1 ml:1 ml) system. ^t TLC system: cellulose/isobutanol–tetrahydrofuran–water–acetone–*p*-toluenesulphonic acid (8 ml:6 ml:5 ml:1 ml:0.3 g) system. ^w TLC system: cellulose/butanol–acetic acid–water (12 ml:3 ml:5 ml) system.

which show for the first time that compounds lacking a sulphur atom in their molecules are also able to induce this reaction.

2. Experimental

2.1. Materials and reagents

All chemicals used were prepared according to Refs. [12–14] or were purchased from Aldrich (Milwaukee, USA).

The iodine–azide, DDQ, ninhydrine (Nin.) and molybdate (Mo) reagents were prepared and used according to Ref. [8]. Manganate reagent (Mn) was a 2% aqueous solution of potassium permanganate.

2.2. Determination of the induction activity

Determination of the induction activity of the phosphoryl derivatives 1a, 1e, 2b, 2e, 7 and 8 in the induced iodine–azide reaction (in solution) was carried out in accordance with the procedure described in Refs. [7,9].

2.3. Thin-layer chromatography

Pre-coated silica gel 60 F₂₅₄ aluminum sheets or pre-coated aluminum oxide 60 F₂₅₄ aluminum sheets or plates RP-18 F₂₅₄ (all 10 cm × 5 cm), with a 0.2 mm thick layer (Merck, Darmstadt, Germany), were used for TLC experiments. The plates were spotted with an appropriate amount of compound (see Table 1), developed for a distance of 8 cm with the solvent, air dried and sprayed with a freshly prepared 1:1 mixture of sodium azide and iodine solutions [8].

3. Results and discussion

The results on the TLC detection of the broad spectrum of representative classes of organophosphorus derivatives are presented in Table 1. These data illustrate the possibilities of TLC differentiation of organophosphorus compounds containing tri- and pentavalent phosphorus.

The most unusual effect was obtained during the TLC application of the iodine–azide detection re-

agent. As a matter of fact, some trivalent phosphorus derivatives induced the iodine–azide reaction on silica oxide TLC plates in a manner similar to typical sulphur containing inductors. Thus, the unexpected detection of trivalent phosphorus derivatives by means of the iodine–azide reagent presents as white spots on the yellow background. This can be explained by the induction of the iodine–azide reaction in spots occupied by “active” phosphorus compounds. This unexpected phenomenon constitutes the first example of the induction of an iodine–azide reaction caused by the compounds which do not contain sulphur in the molecule. The sensitivity of the detection has been dependent on the structure of the phosphorus compounds applied and on the type of TLC plates used. Thus, triphenyl phosphine (5a) is detected as a white spot if the detection is carried out on silica oxide plates, or brown spots are formed on alumina oxide and/or on reversed-phase plates.

These results led us to investigate the induction of the iodine–azide induced reaction by phosphoryl inductors in solution (see Section 2). However, in spite of the distinct induction activity of these phosphoryl derivatives that were exhibited on the TLC plates (Table 1), they were totally inactive for reactions carried out in solution.

Recapitulating, the selectivity of the iodine–azide reagent in the TLC detection of thiophosphates [8,10,11] is diminished by interference of sulphur-containing compounds [1–6] and also by some phosphoryl derivatives. The knowledge that the scope of action of the iodine–azide reagent is not limited to sulphur containing compounds only should be taken into consideration in further analytical applications of this reagent.

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