CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF PHOSPHORUS COMPOUNDS

PART VIII. THE ACID HYDROLYSIS OF SODIUM TRIMETAPHOSPHIMATE WITH REFERENCE TO RING STABILISATION

F. H. POLLARD, G. NICKLESS AND A. M. BIGWOOD

Department of Chemistry, The University, Bristol (Great Britain)

(Received December 20th, 1962)

Recent investigations[1–3] into the mechanism of the hydrolysis of sodium trimetaphosphimate (TMPm), have shown that the replacement of the three imido-linkages by oxygen, takes place in a regular sequence, yielding the corresponding ring phosphates, *i.e.* diimido-trimetaphosphate (DITMP), monoimidotrimetaphosphate (ITMP), and trimetaphosphate (TMP). POLLARD, NICKLESS AND WARRENDER[3] have shown that the replacement of the individual imido-linkages by oxygen takes place without the intervention of intermediate unstable chain imidophosphates, and that the ring phosphate becomes increasingly stable as oxygen replaces the imido-groups.

Ion-exchange chromatographic separations of TMPm, DITMP, ITMP, and TMP have been developed to yield completely separated fractions of each phosphorus-bearing species. This paper reports the evaluation of the reaction kinetics of the hydrolysis reaction, and the relative stabilities of these closely related compounds.

EXPERIMENTAL

Sodium trimetaphosphimate

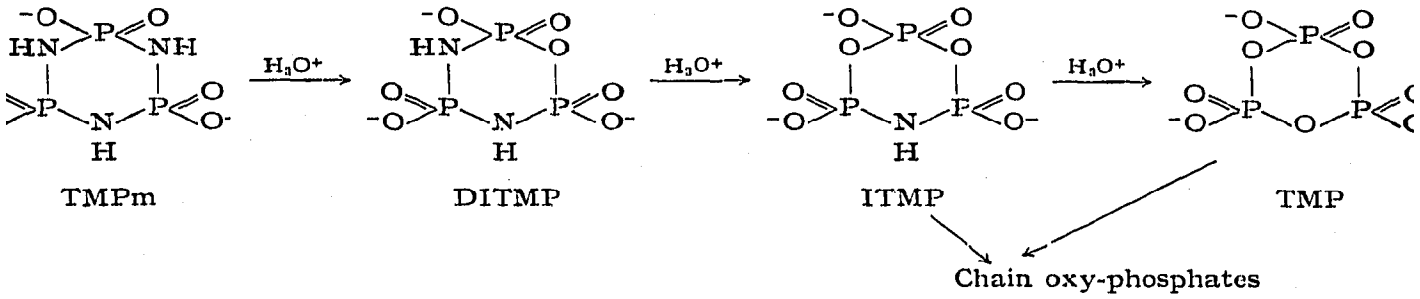
Preparation. Sodium trimetaphosphimate can be prepared by the hydrolysis of the trimeric phosphonitrilic chloride dissolved in diethyl ether, using sodium acetate solution as the aqueous hydrolytic medium, following the method described by STOKES[4]. However, on repetition of STOKES' method it was found to suffer the serious disadvantage that since diethyl ether and water are immiscible, the time of reaction has to extend to four or five days, and furthermore, reaction yields were found to be low.

To overcome these difficulties, dioxan was used as solvent for the trimeric phosphonitrilic chloride, and caustic soda solution was used as the hydrolytic medium. Since dioxan and water are miscible, the reaction time was decreased to about six hours. A typical preparation was as follows:

30 g of trimeric phosphonitrilic chloride was dissolved in 170 ml dioxan, and poured into a solution of 6 *N* caustic soda solution (150 ml). The mixture was gently agitated by stirring for six hours at room temperature, the contents of the reaction vessel gradually solidified. The products of the reaction, TMPm, sodium chloride, and sodium orthophosphate were filtered off, washed with a 60–40 % methanol–water solution, in which only TMPm is insoluble. After repeated washings, the prod-

uct was dissolved in water, and reprecipitated by slowly adding methanol. Filtration, and final washing with methanol, yielded a white compound which was pure sodium trimetaphosphimate. The salt was characterised by the normal methods, analysis, potentiometric titration, infra-red, and gave a single peak, the retention volume of which corresponded to TMPm.

Detection, and determination of hydrolysis products. It has been shown that in acid solution[3], TMPm breaks down to yield DITMP, which hydrolyses in turn to ITMP, which subsequently hydrolyses to TMP and chain oxy-phosphates.



Thus for elucidation of the kinetics of the reaction, a method of analysis for TMPm, DITMP, ITMP, TMPm and orthophosphate is required. POLLARD, NICKLESS AND WARRENDER[3], published such a separation but by refinement of the anion-exchange technique, using Dowex-1 resin (1 × 8) of mesh size 100–200, packed into a column 50 cm long, and 0.9 cm diameter, and eluting the phosphate species with a gradient chloride solution of 0.75 *M* potassium chloride pH 5 dropping into 0.075 M potassium chloride pH 5[3,5], the type of separation obtained is shown in Fig. 1. Each species was estimated using the phosphovanadomolybdate method for phosphorus analysis[6], after hydrolysis to orthophosphate[3].

The retention volumes (position of peak maximum) were:

Orthophosphate	70 ml
Trimetaphosphimate	270 ml
Diimidotrimetaphosphate	370 ml
Monoimidotrimetaphosphate	490 ml
Trimetaphosphate	730 ml

The sharpness of the elution peaks, enabling complete fractions to be isolated, was mainly due to the very slow flow-rates (30 ml/h) and the very steep chloride gradient. Higher flow rates and lower chloride gradients were both found to "spread" the peaks. The yield of phosphorus recovered from each peak was always within 1–2 % of the theoretical quantity when using known mixtures.

Kinetics of hydrolysis of TMPm at pH 3.62. The hydrolysis of TMPm was studied at two different temperatures, 52° and 65°.

Approximately 0.5 g of TMPm was dissolved in 50 ml of a sodium acetate–hydrochloric acid buffer pH 3.62, in a 100 ml graduated flask, containing a loosely fitting stopper. The flask was immersed in a water-bath, thermostatically controlled at the required temperature, at a noted time. At various time intervals, 5 ml samples of the hydrolysing solution were quickly removed from the reaction vessel and poured into a 10 ml graduated flask, containing 5 ml of ice cold 0.1 *N* caustic soda solution.

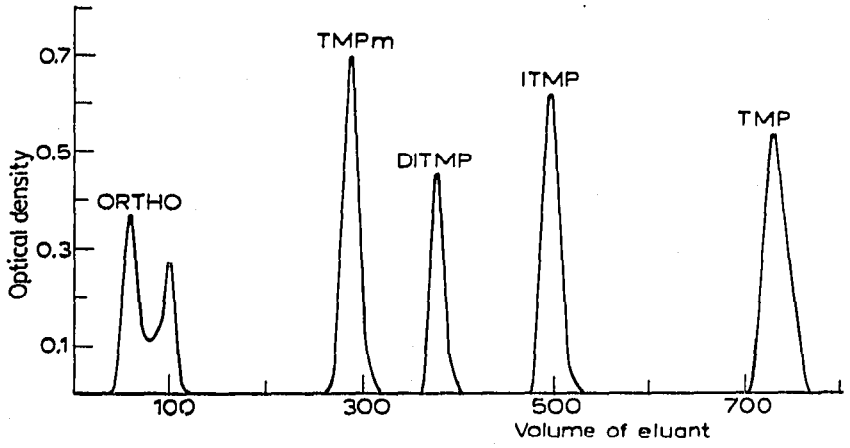


Fig. 1. Separation of orthophosphate, trimetaphosphimate (TMPm), diimidotrimetaphosphate (DITMP), imidotrimetaphosphate (ITMP), and trimetaphosphate (TMP).

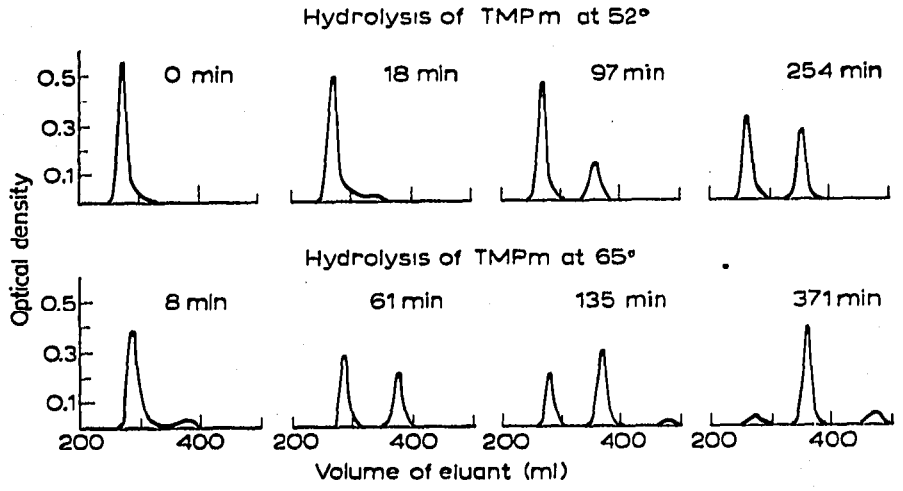


Fig. 2. Elution patterns for the hydrolysis of trimetaphosphimate at pH 3.6.

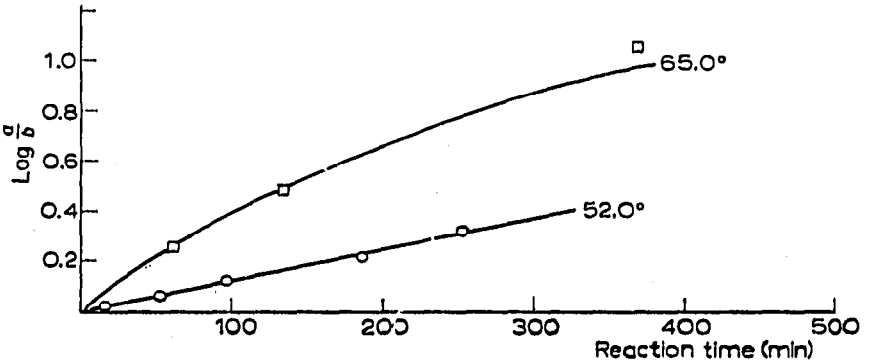


Fig. 3. Variation of log a/b with time for the hydrolysis of trimetaphosphimate at pH 3.6. a = concentration of TMPm at T = 0 min; b = concentration of TMPm at T = t min.

The flask was surrounded by water at 0°. This procedure "freezes" the reaction at the noted time interval, and the contents of the flask remain unreactive and at constant proportions for several days under these conditions.

To analyse the mixture, a 1 ml sample is pipetted on to the anion-exchange column, and the elution allowed to take place, in the manner as described previously. Fig. 2 shows the course of the reaction at 52° and at 65° respectively, using the scheme above.

TABLE I

VELOCITY CONSTANTS OF TMPm DEGRADATION

52°		65°	
Time of reaction (min)	*$k \times 10^3$ (min^{-1})*	*Time of reaction (min)*	*$k \times 10^3$ (min^{-1})*
19	2.25	62	9.41
47	3.05	136	8.01
97	2.81	371	6.49
187	2.61		
254	2.78		
$k_{52°} = 2.81 \cdot 10^{-3}\ min^{-1}$		$k_{65°} = 8.91 \cdot 10^{-3}\ min^{-1}$ (using the initial rate of reaction)	

Results. As the total optical density of any one analysed phosphorus species is directly related to the quantity of phosphorus present, it is a simple matter to evaluate the reaction velocity constants (assuming first order kinetics), which are given in Table I and their variation in time in Fig. 3.

Sodium diimidotrimetaphosphate

Preparation and purification. The preparation of sodium diimido trimetaphosphate involving the hydrolysis of sodium trimetaphosphimate as described by STOKES[4] and DE FICQUELMONT[7] are both satisfactory in so far as the product is predominantly DITMP (up to 80 %), but for kinetic studies, they are unsatisfactory as impurities of TMPm and ITMP are certain to occur.

From studies on the hydrolysis of TMPm, it is apparent that the maximum yield of DITMP is obtained after hydrolysing TMPm at pH 3.62, and 65° for 6 h. Lengthier hydrolysis would yield greater impurities of ITMP, whilst shorter hydrolysis times would give TMPm impurities.

It was realised, that the only practical method available of isolating pure DITMP from TMPm and ITMP impurities, was to employ in some manner, the ion-exchange separation. The method which was finally used is as follows:

TMPm, DITMP, ITMP have retention volumes of 270, 370, and 490 ml (± 10 ml) respectively, under the conditions used for the analysis. It is assumed that the phosphate species remained adsorbed at the top of the ion-exchange column until a certain and specific "desorption" chloride concentration is reached, whereupon it exchanges rapidly with the resin and eluant. Thus it travels quickly down the column to be eluted from the column after 30 ml (the dead volume of the column) of the requisite chloride concentration is attained and passes down the column. Now for the different retention volumes of TMPm etc. the actual chloride concentration at these volumes of effluent can be evaluated using the equation:

$$M_t = M_I - (M_I - M_0)e^{-rt/v}$$

where M_0 = molarity of KCl solution in mixing bottle initially (moles/l)
M_t = molarity of KCl in mixing bottle at time t (min) (moles/l)
M_I = molarity of KCl in reservoir (moles/l)
r = rate of flow of eluant (ml/min)
v = volume of solution in mixing bottle (ml)

The various chloride concentrations calculated are shown in Table II.

0.5 g of a mixture of imido-phosphates containing approximately 14 % TMPm, 75 % DITMP, and 16 % ITMP was dissolved in 50 ml 0.226 *M* potassium chloride

TABLE II

Species	*Concentration of KCl (moles/l)*
TMPm	0.226
DITMP	0.278
ITMP	0.325

solution and adsorbed on to a column of Dowex-1 resin 50 cm long and 12 cm diameter.

The phosphate mixture was obtained by hydrolysing 0.5 g TMPm dissolved in 50 ml sodium acetate–hydrochloride acid buffer pH 3.62 at 65° for 6 h. The phosphate species were precipitated from solution using an ethanol–water solution (2:1), washed thoroughly with pure ethanol, and dried under vacuo. The column was previously equilibrated with 50 ml of 0.226 *M* potassium chloride solution buffered to pH 5.0 by a citric acid–caustic soda solution. After absorption of the imido-phosphates, a further 50 ml of 0.226 *M* potassium chloride solution was passed through the column to remove the TMPm. 120 ml of 0.278 *M* potassium chloride buffered to pH 5 were now passed through the column, and the effluent was allowed to drop directly into a large volume of methanol, whereupon the DITMP was precipitated out. Filtration, washing with ethanol, drying under vacuo produced a white powdery solid, which on examination was found to be DITMP only. Analysis, potentiometric titration, and especially anion-exchange showed only one phosphorus species to be present, with no detectable amounts of TMPm or ITMP (*i.e.* less than 0.5 %). The yield of pure DITMP was of the order of 45 %.

Kinetics of hydrolysis of DITMP at pH 3.62. Using exactly similar procedures to those used for the TMPm hydrolyses reactions, a study of the hydrolysis of DITMP

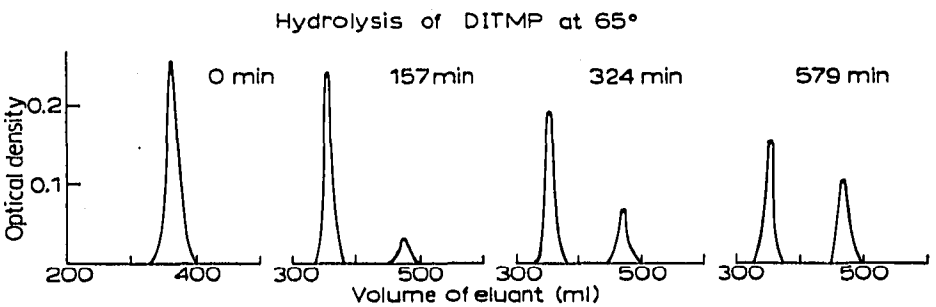


Fig. 4. Elution patterns for the hydrolysis of diimidotrimetaphosphate at pH 3.6 and 65°.

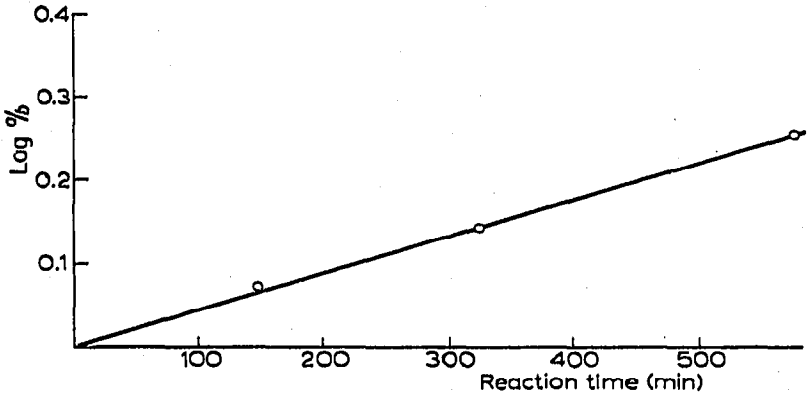


Fig. 5. Variation of log a/b with time for the hydrolysis of diimidotrimetaphosphate at 65° and pH 3.6. a = concentration of DITMP at T = 0 min; b = concentration of DITMP at T = t min.

was made, however, only at one temperature 65° because of the greater stability of DITMP as compared to TMPm. The results are shown in Figs. 4 and 5, and assuming first order kinetics, the velocity constants are given in Table III.

TABLE III

VELOCITY CONSTANTS OF DITMP DEGRADATION AT 65°

Time of reaction (min)	$k \times 10^{-3}$ *(min^{-1})*
157	1.05
324	1.01
579	1.01
1294	0.90

Sodium monoimidotrimetaphosphate

Preparation and purification. The preparation of sodium monoimidotrimetaphosphate by the acid hydrolysis of TMPm[8], yields a moderately pure product, but again, one which is contaminated by its immediate decomposition products, and by DITMP from which it is actually formed.

ITMP was prepared by dissolving 10 g of sodium trimetaphosphimate in a 5:1 vol./vol. water–glacial acetic acid solution, and heating the solution to 50° for 150 h. Paper chromatographic analysis of the reaction solution showed the presence of orthophosphate, ITMP and TMP. The ITMP was precipitated from solution with ethanol, leaving the orthophosphate and TMP in solution. The product was washed thoroughly with ethanol, redissolved in a minimum (20 ml) of water, filtered and re-precipitated with ethanol. The dried product, when examined by anion-exchange chromatography, showed the presence of traces of TMP, DITMP and orthophosphate, therefore it was necessary to purify the ITMP. The calculated chloride concentration for desorption from the exchange column is 0.325 M potassium chloride solution. Using this value and an exactly similar procedure to that described for the DITMP purification, a pure sample of ITMP was prepared. Ion exchange and paper chromatographic analysis showed the final product to be 100 % pure ITMP.

Kinetics of hydrolysis of ITMP at pH 3.62. Identical methods of procedure were used for studying the hydrolysis of ITMP as was used for the hydrolysis of DITMP.

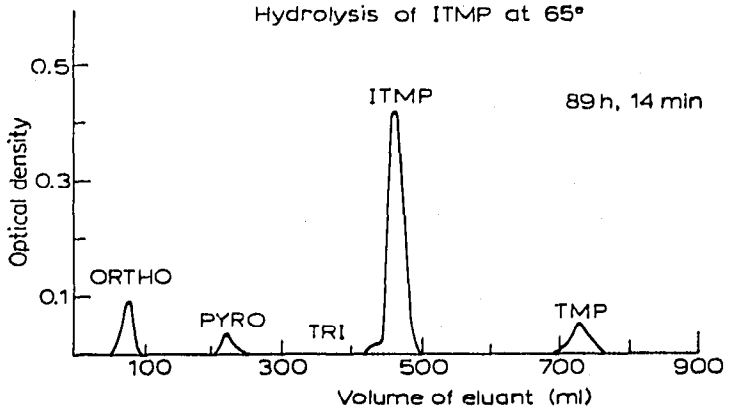


Fig. 6. Elution pattern for the hydrolysis of monoimidotrimetaphosphate at 65° and at pH 3.62 after nearly 3 days reaction time.

The results are shown in Fig. 6. ITMP is hydrolysed by two mechanisms[3]:

(i) Replacement of the final –NH– group linkage by oxygen.

(ii) Degradation of the ring structure to chain oxy-phosphates.

Assuming first order kinetics for both processes the following results are obtained and are shown in Table IV.

TABLE IV

VELOCITY CONSTANTS OF ITMP DEGRADATION AT 65°

Time of reaction (min)	*Velocity constant*	
	Chain species (min^{-1})	*Ring species (min^{-1})*
469	No reaction	
1,025	$4.6 \cdot 10^{-5}$	Undetected
3,720	$4.3 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$
5,354	$4.2 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$

DISCUSSION

The evaluation of the k_{TMPm} velocity constants for the hydrolysis of TMPm, at 65°, and 52°, leads to an estimation of the activation energy E^*_{TMPm} (Fig. 7). The point at $I/T = 0.0030$ is from the data of POLLARD, NICKLESS AND WARRENDER[3]. $E^*_{TMPm} = 19.5$ kcal/mole^{-1}. Assuming now that the constant A in the equation:

$$\log k = \log A - \frac{E^*}{RT}$$

is constant for the closely related series of compounds TMPm, DITMP and ITMP, then the activation energies of the latter two compounds can also be calculated and are given in Table V.

The replacement of one imido-linkage in a six-membered ring, by an oxygen atom stabilizes the ring by 1.45 kcal/mole. It might be logically deduced, that the ring phosphate by the further replacement of an imido-linkage by oxygen would be stabilized by a further factor of 1.5 kcal/mole, and this is in fact shown by the figures. Furthermore, kinetic studies on the hydrolysis of trimetaphosphate in acid solution[9], evaluate E^*_{TMP} to be 24.0 kcal/moles^{-1}, a stabilisation increase of 1.5 kcal/mole over

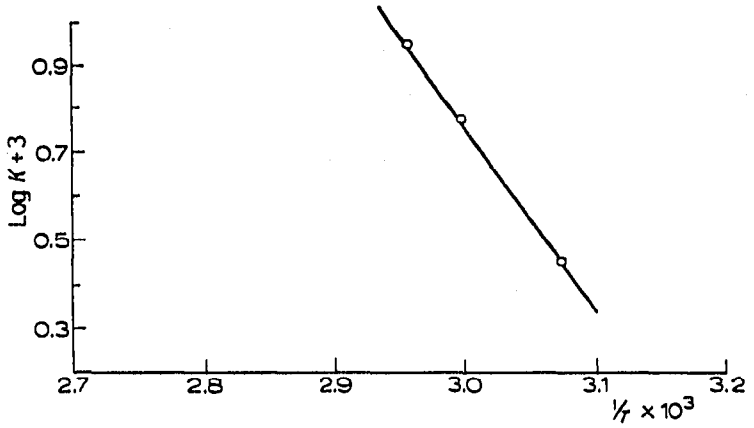


Fig. 7. Variation of reaction velocity K for the hydrolysis of trimetaphosphimate at pH 3.62 with temperature.

ITMP. Thus there appears to be a remarkably consistent stabilisation factor of 1.5 kcal/mole in the series trimetaphosphimate to trimetaphosphate, as each imido-linkage is successively replaced by oxygen.

TABLE V

REACTION CONSTANTS OF IMIDOMETAPHOSPHATES

Species	*Velocity constant at 65° (min⁻¹)*	*E* (kcal/mole)*	*Differences (kcal/mole)*
TMPm	$8.91 \cdot 10^{-3}$	19.5	1.45
DITMP	$1.02 \cdot 10^{-3}$	20.9(5)	1.45
ITMP	$2.30 \cdot 10^{-5}$	22.5	

ACKNOWLEDGEMENT

The authors wish to thank the Department of Scientific and Industrial Research for a Research Studentship to A. M. BIGWOOD, during the tenure of which the research was carried out.

SUMMARY

A kinetic study of the hydrolysis of the series trimetaphosphimate, diimidotrimetaphosphate, monoimidotrimetaphosphate is described, where the products of reaction are determined by a combination of gradient elution anion exchange chromatography and colorimetry. Reaction velocity constants are determined, and observations concerning the ring stabilisation are discussed.

REFERENCES

1 A. NARATH, F. H. LOHMAN AND O. T. QUIMBY, *J. Am. Chem. Soc.*, 78 (1956) 4493.
2 A. NARATH, F. H. LOHMAN AND O. T. QUIMBY, *J. Am. Chem. Soc.*, 82 (1960) 1089.
3 F. H. POLLARD, G. NICKLESS AND R. W. WARRENDER, *J. Chromatog.*, 9 (1962) 493.
4 H. W. STOKES, *Am. Chem. J.*, 18 (1896) 630.
5 J. E. GRANDE AND J. BEUKENKAMP, *Anal. Chem.*, 28 (1956) 1497.
6 R. E. KITSON AND M. G. MELLON, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 379.
7 A. M. DE FICQUELMONT, *Ann. Chim.*, 12 (1939) 169.
8 O. T. QUIMBY, A. NARATH AND F. H. LOHMAN, *Document No. 6013*, ADI Auxiliary Publication
9 Project, Library of Congress, Washington, D.C. (1960).
M. HEALY AND M. L. KILPATRICK, *J. Am. Chem. Soc.*, 77 (1955) 5258.