

New aspect of the mechanism of photocatalytic oxidation of organic compounds by polyoxometalates in aqueous solutions. The selective photooxidation of propan-2-ol to propanone: The role of OH radicals

Athanasios Mylonas,^a Anastasia Hiskia,^a Evaggelia Androulaki,^{ab} Dimitra Dimotikali^b and Elias Papaconstantinou^{*a}

^a Institute of Physical Chemistry, NCSR Demokritos, 153-10 Athens, Greece

^b Chemical Engineering Department, NTU, 157 80 Athens, Greece

Received 19th October 1998, Accepted 8th December 1998

The excited state of polyoxometalates, (POM) arising from absorption of light at the O → M charge transfer (CT) band (near-VIS and UV light), is a powerful oxidizing reagent. The oxidizing ability is manifested, mainly, through formation of OH radicals arising from the reaction of the excited POM with adsorbed water. The currently accepted mechanism of H-abstraction as the initial reaction of excited POM with organic substrates (mainly alcohols) is modified by addition of one more step that involves the formation of OH radicals which, as is well known, react with organic substrates, mainly alcohols, by H-abstraction. In view of the formation of OH radicals, and the high oxidizing ability of the excited POM, the photochemical selective oxidation of organic substrates, reported so far, in aqueous solutions, should be considered with reservation. Propan-2-ol is, indeed, selectively oxidized to propanone in the presence of $\text{PW}_{12}\text{O}_{40}^{3-}$. The selectivity is, however, a kinetic phenomenon rather than a thermodynamic one. Both photoreactions, as is the case with numerous other organic compounds, give, as final products, CO_2 and H_2O .

Introduction

POMs are oligomeric, well defined, metal oxygen cluster anions, produced by acid condensation of mononuclear metal oxide anions, mainly molybdates and tungstates in their d^0 electronic state.¹ Besides their well defined structures that serve as models for theoretical studies, they are also of diverse practical interest. Numerous applications involve analytical chemistry, biochemistry,² electrochromism,³ microelectronics⁴ etc. However, by far the most important application of POMs is in the field of catalysis.⁵

POMs undergo step-wise “reversible” redox reactions, acting as multielectron and oxygen relays. Absorption of light at the O → M CT bands (near-VIS and UV light) enhances their oxidizing ability rendering them powerful oxidizing reagents able to oxidize a great variety of organic compounds.⁶

Although the first paper on the photochemistry of POMs appeared a long time ago,⁷ it has only been in the last 20 years or so, that the field has experienced considerable growth.^{6,8}

The primary photochemical reaction results in the oxidation of organic compounds and the concomitant reduction of the POM. Although there have been indications of electron transfer (ET), in the primary photochemical reaction,⁹ most authors seem to accept the hydrogen-abstraction mechanism.⁶ Molecular orbital studies by the groups of Anderson and Hill, using, mainly, $\text{W}_{10}\text{O}_{32}^{4-}$, support the H-abstraction mechanism, although ET followed by protonation could not be ruled out, especially in polar media.¹⁰

The purpose of this paper is: (a) To verify and at the same time improve the existing accepted mechanism of hydrogen abstraction, in the primary photochemical reaction of POM, with mainly alcohols, by adding one more step that involves the formation of OH radicals. (b) To show, in view of the above observation, *i.e.* formation of OH radicals as well as the

high oxidizing ability of the excited POM, that photochemical selectivity with POM, in aqueous solutions, reported so far in the literature, is a thermodynamic one. (c) To reexamine the “selective” photooxidation of propan-2-ol to propanone by POM.

Experimental

$\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{W}_{10}\text{O}_{32}^{4-}$ were prepared according to literature methods.¹¹ All chemicals used were of analytical grade. $\text{PW}_{12}\text{O}_{40}^{3-}$ is, practically, stable in aqueous solution at pH 1, whereas, $\text{W}_{10}\text{O}_{32}^{4-}$ is stable for days at pH 2.5.

An Oriel 1000 W Xe lamp was used for photolysis, with a water filter to avoid overheating the solution from the near-IR radiation and 320 and 345 nm filters to avoid possible direct photolysis of the organic substrate. The incident radiation was reduced to *ca.* 40% with a slit diaphragm. In some earlier experiments, a high-pressure Hg arc with a Pyrex filter was used.

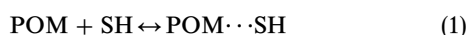
Acetone was analysed in a Hewlett-Packard 5890 II Gas Chromatograph, equipped with an FID and a 10% Carbowax 20 M on Chromosorb W 60/80 mesh 2 m column. Gas samples were analysed for CO_2 in a VARIAN 3300 Gas Chromatograph equipped with a TCD and a Porapack Q 2 m column. Carbon dioxide was calculated from a standard curve, determined under identical conditions using known quantities of CO_2 as follows: 4.0 ml of aqueous solutions, 0.1 M HClO_4 , were added to a photolysis cell, total volume 8 ml. After 20 min oxygenation, the cell was covered with a serum cap. A micro-syringe was used to introduce small volumes of Na_2CO_3 standard solutions (2×10^{-3} , 2×10^{-2} and 0.2 M). After stirring the mixture, 1 ml of the gas phase was analysed in the GC with TCD. The results were expressed as concentration of CO_2 in 4 ml solution. The calibration curve was linear from $0.5\text{--}40 \times 10^{-4}$ M with a correlation coefficient >0.98 .

The degree of reduction of POM in photolysed deaerated solutions was calculated from the known molar absorption coefficients of the blue products, using a Perkin Elmer Lambda 19 spectrophotometer.¹¹

Unless otherwise stated, a typical experiment was as follows: To an 8 ml spectrophotometric cell, 1 cm in length, covered with a serum cap, 4.0 ml solution of catalyst and substrate was introduced. Photolysis was performed with constant stirring at 20 °C, the pH was adjusted with HClO₄. Deaerations and oxygenations were performed with extra-pure Ar and dioxygen. Solution samples were withdrawn at time intervals and analysed for products.

Results and discussion

Upon dissolution of POM and organic substrate in water, all data suggest that a preassociated complex, or preassociated equilibria, or for that matter a supramolecular species, is formed.



This has been substantiated, as stated before, from the following: (a) The rate constants of excited POM with organic substrates which were reported to be *ca.* 10¹² dm³ mol⁻¹ s⁻¹,¹² *i.e.* faster than diffusion controlled, (b) NMR data,¹² (c) crystal structures of a variety of organic-POM associated complexes¹³ and (d) the Langmuirian behaviour of the system.^{6,14}

Water molecules also participate in the associated complex and they react with the excited catalyst, producing OH radicals, see reaction (5), below. The existence of OH radicals suggests a modification of the mechanism and the re-evaluation of the selectivity of photochemical reactions in aqueous solutions reported so far.

1 H-abstraction mechanism

There are two ways in which the excited POM can react with organic substrates in aqueous solution: (a) Direct reaction of the two species and (b) reaction *via* OH radicals.

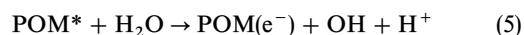
The redox mechanism proposed for the reaction of photo-excited POM with organic substrates, mainly alcohols, is H-abstraction⁶ involving only the direct reaction. In this mechanism, below, two more steps are added [reactions (5) and (6)] that involve H-abstraction through OH radicals.



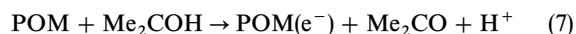
Direct reaction of POM* with substrate (originally proposed)



Indirect reaction of POM with substrate, *via* OH radicals



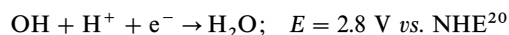
Both direct and indirect reactions produce the hydroxy alkyl radical, Me₂COH, which reacts further with POM



(We have avoided the preassociation complex, reaction (1), for reasons of clarity.) This mechanism, that originally did not involve reactions (5) and (6), was deduced from the fact that only species with easily removable hydrogens, *i.e.* primary and secondary alcohols, act as effective photoreducing reagents for POM, whereas, *tert*-butyl alcohol was considerably less effective,⁶ and a deuterium isotope effect *k_H/k_D* ≈ 3.7 in the production of acetone, when deuterated Me₂CDOH was used.¹⁵ Reaction (7) was justified by independent experiments that generated hydroxy alkyl radicals through ⁶⁰Co-γ-radiation,¹⁶

whereas, a variety of oxidants close the photocatalytic cycle.⁶ Now, it appears that the same data, that support the direct H-abstraction *via* POM*, support also indirect H-abstraction *via* OH radicals: reactions (5) and (6).

The formation of OH radicals during photolysis with POM in aqueous solutions [reaction (5)] has been suggested by: (a) Detection of OH adducts (hydroxylation products) in photolysis experiments with aromatic hydrocarbons,^{17,18} (b) EPR trapping techniques,¹⁹ and (c) the fact that the excited state potentials of practically all POM are more positive than the reaction



The excited-state potential of POM can be calculated from the equation: [excited-state potential of POM (V vs. NHE)] = [ground-state reduction potential of POM (V vs. NHE) + 1240/(0-0) transition energy], where the (0-0) transition energy is, roughly, the threshold absorption (nm) of the O → M CT band in the near-VIS region. Thus, the threshold absorption of *ca.* 400 nm, which is usual for POMs, enhances their oxidizing ability by *ca.* 3 eV.

Now, OH radicals are known to react with alcohols, with α-hydrogens, by H-abstraction, with diffusion-controlled rates,²¹ reaction (6). Thus the originally proposed mechanism⁶ is modified with one more step that involves H-abstraction *via* OH radicals.

No overall distinction between direct and indirect H-abstraction is possible with regular photoredox experiments in aqueous solution. Note that addition of reactions (5) and (6) gives the originally proposed reaction (4).

2 Selective vs. non-selective oxidation

In view of the evidence for OH radical formation during photolysis of POM in aqueous solution and the high oxidizing ability of excited POM, any reported selective oxidation of organic substrates in aqueous solution ought to be considered with reservation. The results, so far, have shown that excited POMs are able to cause photodegradation to CO₂ and H₂O, of a great variety of organic compounds.¹⁷ Thus “selectivity” is a kinetic phenomenon (competition kinetics) rather than a thermodynamic one.

2.1 Photooxidation of Me₂CHOH by PW₁₂O₄₀³⁻. One case is worth mentioning: the photocatalytic selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones by POM.⁶ It was stated that ethanol is selectively oxidized to ethanal in the presence of SiW₁₂O₄₀⁴⁻.²² In view of our recent results indicating the formation of OH radicals, we decided to re-examine the “selective” photooxidation of alcohols.²³

We have re-examined the system propan-2-ol and propanone in the presence of PW₁₂O₄₀³⁻. Fig. 1 shows the variation of the initial rate of oxidation of deaerated solutions of propan-2-ol and the variation of the initial rate of oxidation of deaerated solutions of propanone in the presence of PW₁₂O₄₀³⁻, upon photolysis of the system with λ > 320 nm. As is known, in the absence of dioxygen, no re-oxidation of reduced 12-tungstophosphate takes place, at least in the first stages of the reduction, so that the progress of the reaction could be followed by the development of the blue colour of reduced tungstate, PW₁₂O₄₀⁴⁻. Fig. 2 shows the development of the final product, CO₂, produced from the photooxidation of propanone.

From Fig. 1 and 2, one may observe the following: propan-2-ol is photooxidized, as is well established, to propanone. Propanone is further oxidized with a rate that, except for very low concentrations (inset of Fig. 1), is two orders of magnitude slower than the photooxidation of propan-2-ol. The final photodegradation product of propanone, checked at 1.0 mM

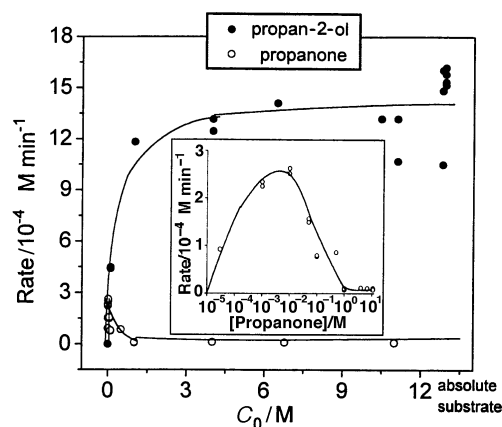


Fig. 1 Comparison of the variation of the initial rates of formation of reduced 12-tungstodiphosphate ($\text{PW}_{12}\text{O}_{40}^{3-}$) with concentration of substrate, upon photolysis, $\lambda > 320$ nm, of deaerated aqueous solution of $\text{PW}_{12}\text{O}_{40}^{3-}$ in the presence, separately, of propan-2-ol and propanone. $\text{PW}_{12}\text{O}_{40}^{3-}$ 0.7 mM, pH 1 (HClO_4), $T = 20^\circ\text{C}$. Inset: Details of the photooxidation of propanone at low concentrations.

and 0.1 M of propanone is CO_2 , as is the case with numerous aliphatic and aromatic compounds that degrade to CO_2 , H_2O and inorganic anions.¹⁷

Fig. 2 shows that the oxidation of propanone is quantitative,

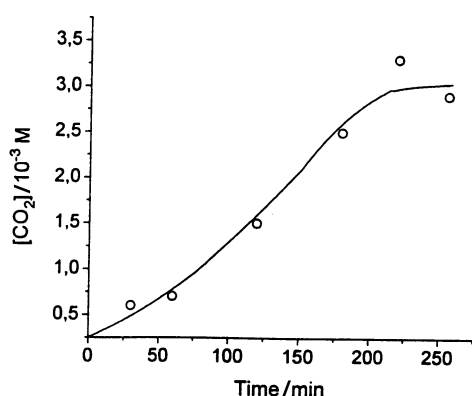
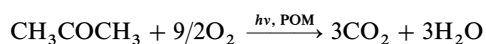


Fig. 2 Evolution of CO_2 upon photodegradation of oxygenated aqueous solution of propanone, in the presence of $\text{PW}_{12}\text{O}_{40}^{3-}$. $\text{PW}_{12}\text{O}_{40}^{3-}$ 0.7 mM, propanone 1.0 mM, $\lambda > 320$ nm, pH 1 (HClO_4), $T = 20^\circ\text{C}$.

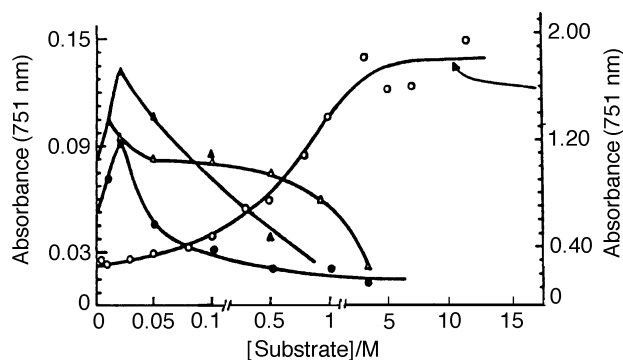


Fig. 3 Variation of absorption (750 nm) of reduced 12-tungstodiphosphate ($\text{PW}_{12}\text{O}_{40}^{3-}$) with concentration of substrate, upon photolysis, for a certain time, of deaerated aqueous solution of $\text{PW}_{12}\text{O}_{40}^{3-}$ in the presence of L(+)-alanine and *tert*-butyl alcohol, as well as propan-2-ol and propanone for comparison. (\blacktriangle) L(+)-Alanine, photolysis time 15 min, $\text{PW}_{12}\text{O}_{40}^{3-}$ 0.1 mM; (\bullet) propanone, photolysis time 15 min, $\text{PW}_{12}\text{O}_{40}^{3-}$ 0.1 mM; (\triangle) *tert*-butyl alcohol, photolysis time 6 min, $\text{PW}_{12}\text{O}_{40}^{3-}$ 0.1 mM; (\circ) propan-2-ol, photolysis time 3 min, $\text{PW}_{12}\text{O}_{40}^{3-}$ 4 mM. High-pressure Hg arc lamp, Pyrex filter, pH 1 (HClO_4).

No CO_2 is detected after 3 h photolysis under the same conditions but in the absence of $\text{PW}_{12}\text{O}_{40}^{3-}$.

The differences in the rates of photooxidation of propan-2-ol and propanone are in accordance with the differences in the rates of reactions of OH radicals with these two species. It has been long known that OH radicals, produced by ^{60}Co - γ -radiation of aqueous solution, react with propan-2-ol and propanone with rate constants that differ by two orders of magnitude.²⁴ Therefore, the selectivity observed in the oxidation of propan-2-ol to propanone, is a kinetic phenomenon and not a thermodynamic one, because, as mentioned earlier, propanone is further photooxidized by $\text{PW}_{12}\text{O}_{40}^{3-}$ to CO_2 and H_2O , as is the case for numerous other organic compounds.¹⁷

We have stated earlier, that the rate of reaction of the excited catalyst with substrate is, primarily, the result of two competitive reactions: (a) Direct reaction of the two species and (b) reaction of the two species *via* OH radicals. A major point† for consideration is the ratio of the rates

$$k(\text{OH} + \text{Me}_2\text{CHOH})/k(\text{POM}^* + \text{Me}_2\text{CHOH})$$

This ratio can be measured in the presence and absence of water. From Fig. 1, the initial rate of oxidation of alcohol increases as the concentration of propan-2-ol in water increases, reaching a peak at *ca.* 3 M. The rate then remains constant, even in absolute propan-2-ol. At this point, there is no water and, therefore, no OH radicals and the reacting species ought to be POM^* and propan-2-ol. From Fig. 1, this rate $k(\text{POM}^* + \text{Me}_2\text{CHOH})$ is *ca.* $1.3 \times 10^{-3} \text{ M min}^{-1}$ and this is also the maximum rate obtained in the presence of water. Therefore, the ratio $k(\text{OH} + \text{Me}_2\text{CHOH})/k(\text{POM}^* + \text{Me}_2\text{CHOH})$ ought to be close to one. Further, one can consider the rate of the reaction of the excited propanone with propan-2-ol, which is also known to react by H-abstraction.† Absorption experiments with 320 and 345 nm cut-off filters have shown that direct propanone absorption starts to interfere at concentrations of *ca.* 0.5 M, when the 320 nm cut-off filter is used, whereas, with the 345 nm cut-off filter, there is practically no interference, even with propanone. We have performed photooxidation experiments with the 345 nm cut-off filter and found similar results to those with the 320 nm cut-off filter, except that the photooxidation process was slower, since fewer photons are available for excitation of the catalyst.

The general behaviour of the photocatalytic oxidation of organic substrates by $\text{PW}_{12}\text{O}_{40}^{3-}$ is a decrease in the rate of photooxidation, as the ratio substrate/water increases, following peak performance. This may be attributed to the slower direct reaction between the excited $\text{PW}_{12}\text{O}_{40}^{3-}$ and substrate, relative to the reaction *via* OH signals. Such behaviour has been observed in diverse systems *e.g.* *o*-chlorophenol in the presence of $\text{W}_{10}\text{O}_{32}^{4-}$,^{17b} *tert*-butyl alcohol and L(+)-alanine in the presence of $\text{PW}_{12}\text{O}_{40}^{3-}$, shown in Fig. 3, together with propan-2-ol and propanone for comparison.²⁵ Only in the case of propan-2-ol does the rate of direct reaction seem to be competitive with the reaction *via* OH radicals.

Acknowledgements

We thank The Ministry for Development, General Secretariat of Research and Technology for financing part of this work. We also thank one of the reviewers for his helpful suggestions and comments.

References

- (a) M. T. Pope, in *Inorganic Chemistry Concepts*, ed. C. K. Jorgensen *et al.*, Springer Verlag, Berlin, 1983, vol. 8; (b) M. T. Pope and A. Muller, *Angew. Chem. Int. Ed., Engl.*, 1991, **30**, 34;

† Suggested by a referee.

- (c) V. W. Day and W. G. Klemperer, *Science*, 1985, **228**, 533; (d) Q. Chen and J. Zubietta, *Coord. Chem. Rev.*, 1992, **114**, 107.
- 2 (a) A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Wiley, New York, 3rd edn., 1966; (b) H. Wu, *J. Biol. Chem.*, 1920, **43**, 189.
 - 3 R. J. Cotton, A. M. Guzman and J. W. Rabalais, *Acc. Chem. Res.*, 1978, **11**, 170.
 - 4 J. C. Carls, P. Argitis and A. Heller, *J. Electrochem. Soc.*, 1992, **139**, 786.
 - 5 (a) T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, 1996, **41**, 113; (b) I. V. Kozhevnikov, *Catal. Rev. Sci. Eng.*, 1995, **37**, 311.
 - 6 E. Papaconstantinou, *Chem. Soc. Rev.*, 1989, **16**, 1; and references therein.
 - 7 (a) M. Rindl, *S. African J. Sci.*, 1916, **11**, 362; (b) L. Chalkley, *J. Phys. Chem.*, 1952, **56**, 1084.
 - 8 (a) C. L. Hill and C. M. Prosser-McCartha, in *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*, ed. K. Kalyanasundaram and M. Gratzel, Kluwer, Dordrecht, 1993, vol. 14, pp. 307–330; (b) T. Yamase and H. Naruke, *Coord. Chem. Rev.*, 1991, **111**, 83.
 - 9 T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183.
 - 10 (a) M. K. Awad and A. B. Anderson, *J. Am. Chem. Soc.*, 1990, **112**, 1603; (b) S-F. Jen, A. B. Anderson and C. L. Hill, *J. Phys. Chem.*, 1992, **96**, 5658.
 - 11 (a) M. T. Pope and G. M. Varga Jr., *Inorg. Chem.*, 1966, **5**, 1249; (b) A. Chemseddine, C. Sanchez, J. Livage and M. Fournier, *Inorg. Chem.*, 1984, **23**, 2609.
 - 12 M. A. Fox, R. Cardona and E. Gailard, *J. Am. Chem. Soc.*, 1987, **109**, 6347.
 - 13 (a) M. M. Williamson, D. A. Bouchard and C. L. Hill, *Inorg. Chem.*, 1987, **26**, 1436; (b) C. L. Hill, D. A. Bouchard, M. Kadkhodayan, M. M. Williamson, J. A. Schmidt and E. F. Hilinski, *J. Am. Chem. Soc.*, 1988, **110**, 5471; (c) C. J. Gomez-Garcia, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Le Magueres, L. Quahab, L. Ducasse, C. Sourisseau and P. Delhaes, *Inorg. Chem.*, 1995, **34**, 4139.
 - 14 H. Einaga and M. Misono, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1551.
 - 15 M. D. Ward, J. F. Bradzil and R. K. Grasselli, *J. Phys. Chem.*, 1984, **88**, 4210.
 - 16 E. Papaconstantinou, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2769.
 - 17 (a) A. Mylonas and E. Papaconstantinou, *J. Mol. Catal.*, 1994, **92**, 261; (b) A. Mylonas and E. Papaconstantinou, *J. Photochem. Photobiol. A*, 1996, **94**, 77; (c) A. Mylonas, V. Roussis and E. Papaconstantinou, *Polyhedron*, 1996, **15**, 3201; (d) A. Mylonas, A. Hiskia and E. Papaconstantinou, *J. Mol. Catal.*, 1996, **114**, 191.
 - 18 H. Einaga and M. Misono, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3435.
 - 19 (a) T. Yamase, *Inorg. Chim. Acta*, 1983, **76**, L25; (b) T. Yamase and T. Kurozumi, *J. Chem. Soc., Dalton Trans.*, 1983, 2205.
 - 20 W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, NJ, 2nd edn., 1952, p. 48.
 - 21 A. J. Swallow, *Prog. React. Kinet.*, 1978, **9**, 195, and references therein.
 - 22 V. N. Parmon, K. I. Zamaraev, Boroskov Institute of catalysis, Novosibirsk, Russia, as quoted by J. Higgin in *Chem. Eng. News*, Aug. 5, 1996, p. 28.
 - 23 A. Hiskia and E. Papaconstantinou, *Polyhedron*, 1988, **7**, 477.
 - 24 M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, 1967, **18**, 493.
 - 25 D. Dimotikali, Doctoral Dissertation, University of Athens, 1984, p. 133, (in Greek).

Paper 8/08104B