This article was downloaded by: [University of Toronto Libraries] On: 07 January 2015, At: 00:12 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Toxicological & Environmental Chemistry

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gtec20

Photochemical transformation of maleic anhydride in aqueous solutions

O. Bajt^a, B. Šket^b & J. Faganeli^a

^a Marine Biological Station, Fornače 41, Piran, 66330, Slovenia

^b Department of Organic Chemistry, University of Ljubjana, Aškerčeva 5, Ljubljana, 61000, Slovenia Published online: 19 Sep 2008.

To cite this article: O. Bajt , B. Šket & J. Faganeli (1994) Photochemical transformation of maleic anhydride in aqueous solutions, Toxicological & Environmental Chemistry, 43:3-4, 229-234, DOI: <u>10.1080/02772249409358034</u>

To link to this article: <u>http://dx.doi.org/10.1080/02772249409358034</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sublicensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

PHOTOCHEMICAL TRANSFORMATION OF MALEIC ANHYDRIDE IN AQUEOUS SOLUTIONS

O.BAJT, B. ŠKET* and J. FAGANELI

Marine Biological Station, Fornače 41, 66330 Piran Slovenia *Department of Organic Chemistry, University of Ljubjana, Aškerčeva 5, 61000 Ljubljana, Slovenia

(Received 22 July 1993)

Solutions of maleic anhydride, occurring in the waste water of the organic chemical industry in the Koper area (Slovenia) and subsequently entering the river Rižana and the Bay of Koper (Gulf of Trieste, northern Adriatic), in distilled, riverine and artificial and natural sea water were photolyzed using photochemical reactors and exposure to sunlight. The transformation of maleic anhydride under artificial light proceeds first through hydrolysis to maleic acid and then photochemical isomerization of maleic acid to fumaric acid, its partial decarboxylation and polymerization. The polymeric product formed is complex consisting of chains with methylene and methine groups and these chains connected by ether and ester bonds. The average molecular weights of the polymers formed were distributed in a broad range lower than 4200. The izomerization is inhibited by inorganic ions but DOM has a negligible effect. The quantum yields ranged between 0.03–0.04. The influence of the air atmosphere was negligible.

KEY WORDS: Phototransformation, maleic acid, industrial effluents

INTRODUCTION

The release of industrially derived organic compounds into natural waters is of crucial importance because of their toxic effects, resistance to degradation and accumulation in the aquatic environment. In addition transformation of these compounds could lead to modified substrates of even higher toxicity. Among possible reactions, photodegradation, which is competitive with microbially mediated reactions, is of special importance. In natural waters the absorption of sunlight (especially at UV wavelengths) by dissolved organic and inorganic compounds leads to formation of a variety of transient species (1, 2): excited dissolved organic compounds, hydrogen peroxide, singlet oxygen, hydrated electrons, superoxide ion, organoperoxy radicals, hydroxyl radicals and bromine containing radicals in sea water. These radicals are

^{*}Author to whom correspondence should be addressed

highly reactive and thus play an important role in transformations and degradation of dissolved natural organic compounds (3-5) and organic pollutants (6-11).

The organic chemical industry, producing a variety of compounds, is also the source of maleic anhydride which is introduced by waste waters into rivers and subsequently into estuaries and the coastal sea. This is the case of the organic chemical industry in the Koper area (Slovenia) which produces maleic anhydride.

The aim of this research was to elucidate the photochemical transformations of maleic anhydride in various aquatic media (distilled, riverine, artificial and natural sea waters) using a photochemical reactor and natural sunlight. Special attention was paid to the reaction pathways and kinetics because of their environmental significance.

MATERIALS AND METHODS

Reagents

Analytical grade chemical reagents, mostly from Merck (Germany) were used throughout this work. Maleic anhydride 99.9% was obtained from the Iplas Chemical Company (Koper, Slovenia), Citraconic anhydride was from Aldrich (USA). Double distilled water was used in all experiments. Artificial sea water (35) was prepared by dissolving 23.94 g of NaCl, 5.08 g of MgCl₂, 3.99 g of Na₂SO₄, 1.12 g of CaCl₂, 0.67 g of KCl, 0.20 g of NaHCO₃, 0.10 g of KBr, 0.03 g of H₃BO₃ and 0.03 g of NaF in 1 *l* of double distilled water. Riverine water and artificial and natural (35.5) sea water were filtered through Millipore GS membrane filters of 0.22 μ m pore size.

Photochemical Experiments

0.002 M solutions of maleic anhydride in different aqueous media were irradiated in an immersion well photochemical reactor from Applied Photophysics (England), model RQ 125, equipped with a 125 W medium pressure mercury lamp. This lamp emits predominantly 365–366 nm radiation, with smaller amounts in the UV at 265, 297, 303, 313 and 334 nm, as well as a significant amount in the visible region at 404–408, 436–546 and 577–579 nm. The temperature during the experiment was 25°C. The solutions were purged with N₂ or air. The volume of irradiated solution was 90 ml. Photolysis in sunlight was performed in stoppered quartz tubes 30×2 cm exposed for 10 days at the Meteorological Station Piran in September 1991. Dark controls were wrapped in aluminium foil.

The isolation of reaction product in distilled water was performed by evaporation of irradiated solution to dryness. Internal standard solutions of citraconic anhydride and acetone were added. The first step of isolation of reaction product from other aqueous media was the same as described but to the evaporated residue acetone was added, the pH adjusted to 2–2.5 and additionally stirred for one hour at room temperature. Afterwards, the mixture was filtered, evaporated to dryness and the same quantity of internal standard added. The kinetic studies ware performed by maleic anhydride and fumaric acid disappearance measurements.

Analyses

Analyses were performed using a Varian 2700 GC equipped with FI detector and HP 3396 integrator. The GC column used was 5% OS 138, 1% of H_3PO_4 on 80/100 Chromosorb G AW-DMCS. The injector, column and detector temperatures were 240, 160 and 270°C, respectively. The carrier gas (N₂) flow rate was 20 ml/min. Analyses were also performed by HPLC, consisting of a Milton Roy constametric III metering pump working isocratically and a Milton Roy spectromonitor 3100 UV/VIS detector adjusted at 210 nm. A column, 25 cm long, 6.2 mm i.d., packed with 5 μ m LC diol was used. The mobile phase was a mixture of acetonitrile (5%) in 0.03 M H₃PO₄ at a flow rate of 3 ml/min. Identification of the eluting compounds was performed by comparison of their retention times to those of pure compounds.

¹H and ¹³C spectra of photoproduct were obtained using Varian EM 300 L and Varian VXR 300 NMR spectrometers, respectively. Mass spectra were obtained on an Autospeq mass spectrometer (VG-Analytical, England). Molecular weight distribution was determined by gel permeation chromatography using a Perkin Elmer LC-250 liquid chromatograph, PL gel column and a Perkin Elmer LC-30 differential refractometer and LC-235 diode array.

Quantum yields were measured by a quantum meter equipped with 12 W mercury lamp, using potassium ferioxalate as actinometer.

RESULTS AND DISCUSSION

The photochemical transformation of maleic anhydride, which first hydrolizes to maleic acid in aqueous medium, consists of photochemical isomerization to fumaric acid and subsequent photochemical polymerization according to the pathway depicted in Figure 1. Spectroscopic data from ¹H and ¹³C NMR spectra showed that the product formed is a complex polymer. The ¹H NMR spectrum showed several triplet signals in the range 3.1 - 4.5 ppm and doublet signals in the range 1.25-3.0 ppm with J = 6.6 Hz. The COSY experiment revealed that these signals, belonging to $--CH_2$ -and --CH-groups, are in different chemical environments (different chemical shifts). This is also confirmed by mass spectrum, showing $--CH_2$ - and --CH-fragmentations. The chemical shifts for --CH-groups suggests that the bonding between chains is achieved through etheric and esteric bonds. The formation of polymeric product containing this type of bonding proceeds through several reaction steps, including partial decarboxylation of fumaric acid, hydroxylation of double bonds and subsequent polymerization and polycondensation crosslinking.



Figure 1 Photochemical transformation of maleic anhydride in distilled water.

The average molecular weights of the heterogenous polymeric product formed were distributed in broad range lower than 4200.

The kinetic studies of the photochemical transformations of maleic acid in aqueous media (distilled, riverine, synthetic and natural sea water) under artificial light depicted in Figures 2 to 5, revealed two consecutive first order reactions with different rate constants in different aqueous media, as shown in Table 1. The fastest isomerization was observed in riverine water followed by that in natural and artificial sea water and the slowest in distilled water. The polymerization of fumaric acid starts at the concentration of 0.0006 M. The polymerization rates were different to those of isomerization, showing the fastest reaction rates in distilled water. The quantum yields

Table 1 Rate constants $(k_1, k_2, k_2-f.a.)$ of photochemical transformations of maleic anhydride in distilled (DW), riverine (RW), artificial sea (ASW) and sea water (SW). k_2 -f.a. = rate constant calculated from fumaric acid polymerization curve.

<u> </u>	$k_{1}(s^{-1})$	$k_2(s^{-1})$	k_2 -f.a. (s ⁻¹)	
DW	0.7 10-4	2.7 10-4	2.6 10-4	
RW	2.0 10-4		1.9 10-⁴	
SW	1.4 10-4	0.7 10-4	0.9 10-4	
ASW	0.9 10-4	0.6 10-4		



Figure 2 Photodegradation of maleic anhydride (1) and formed fumaric acid (2) in distilled water.



Figure 3 Photodegradation of maleic anhydride (1) and formed fumaric acid (2) in riverine water.



Figure 4 Photodegradation of maleic anhydride (1) and formed fumaric acid (2) in sea water.

Figure 5 Comparison between the photodegradation of maleic anhydride in artificial (1) and natural sea water (2).

measured for the whole photochemical process ranged between 0.03–0.04. The influence of the air atmosphere on these photochemical reactions was also tested and found to be negligible. The results of the photochemical experiments on the maleic anhydride solutions in distilled water in the summer sunlight showed a slow transformation rate. In ten days exposure only about 3% of the reactant was transformated, considering a total energy of incident solar radiation of 18.6 kJ/cm².

The degradation curves of the photochemical transformations of maleic anhydride showed that isomerization is catalyzed especially by inorganic ions and among them HCO_3^- , Na⁺, Mg²⁺ and especially halides because of the ionic compositional difference between riverine and sea water¹². Dissolved organic matter (DOM) has a minor (~15%) catalytic effect. The polymerization reaction, on the other hand, is inhibited by inorganic ions and it appears again that to a large extent HCO_3^- , halides, Na⁺ and Mg²⁺ ions could be primarily responsible for this effect due to the compositional difference between riverine and sea water¹². A similar inhibition was also observed in photochemical polymerization of phthalic acid producing polyphenyil¹⁰. On the other hand, DOM has, in contrast to the phthalic acid polymerization reaction, negligible effect on the fumaric acid polymerization. The reason for this difference probably lies in the structure and reactivity of humic substances in natural waters, consisting of various aromatic compounds and derivatives in various proportions^{3,13}. It is generally recognized that the humic substances are rich in stable free radicals involved in various polymerization-depolymerization and other reactions with organic molecules. The UV irradiation of fulvic acid, for example, produces a variety of aromatic compounds⁴. These compounds could interfere in the polymerization of phthalic acid but not in that of fumaric acid because of the formation of aliphatic polymer. A similar photochemical hydroxylation and oxidative crosslinking of polyunsaturated fatty acids¹⁴ was proposed by Harvey *et al.*¹⁵ to be an important mechanism for the formation of marine humic substances. The photochemical polymerization of fumaric acid is, therefore, not influenced (enhanced or retarded) by DOM, as observed for photochemical isomerization of maleic acid and other photochemical reactions in natural waters².

CONCLUSIONS

1. 1. 1. 1. 1. 1.

The results of this model study indicate that the photochemical transformation of maleic acid, derived from the hydrolysis of maleic anhydride in effluent water of the organic chemical industry, proceeds by two consecutive first order reactions: first isomerization to fumaric acid and subsequently its partial decarboxylation and polymerization to an aliphatic polymer, containing ether and ester bridges between chains. The isomerization is catalyzed principally by inorganic ions, while the polymerization step is inhibited by inorganic ions but DOM has a negligible influence. Photochemical transformation is not influenced by the presence of the air atmosphere. The reaction rates in sunlight are slow, leading to the conclusion that maleic acid enters the brackish and then sea water photochemically unaltered and that this slow reaction proceeds mostly in sea water medium.

References

- 1. O. C. Zafirou, J. Joussot-Dubien, R. G. Zepp and R. G. Zika, Environ. Sci. Technol., 18, 365 (1984).
- 2. J. Hoigné, In Aquatic Chemical Kinetics (W. Stumm, ed.), (Wiley, New York, 1990), pp. 43-70.
- G. G. Choundry, In The Handbook of Environmental Chemistry (O. Hutzinger, ed.), Vol. 1, Part C (Springer-Verlag Berlin, 1984), pp. 1–24.
- 4. R. J. Kieber, X. Zhou and K. Mopper, Limnol. Oceanogr., 35, 89 (1990).
- 5. S. Klemenova, D. M. Wagnerova, Mar. Chem., 30, 89 (1990).
- 6. M. M. Hwang, R. E. Hodson and R.-F.Lee, Environ. Sci. Technol., 20, 1002 (1986).
- 7. K. Hustert, P. N. Moza and P. Bouyet, Toxicol. Environ. Chem., 31-32, 97 (1991).
- 8. G. Durand, D. Barcelé, S. Albaiges and N. Mansour, Toxicol. Environ. Chem., 31-32, 55 (1991).
- 9. P.Méallier, A. Mamouni and M. Mansour, Chemosphere, 20, 267 (1990).
- 10. O. Bajt, B. Šket and J. Faganeli, Chemosphere, 24, 673 (1992).
- 11. M. G. Ehrhardt, K. A. Burns and M. C. Bicego, Mar. Chem., 37, 53 (1992).

and the state of the

 $\phi_{ij} = \phi_{ij} = \phi_{ij} = \phi_{ij} = \phi_{ij}$

- 12. F. Millero, In Marine Chemistry in the Coastal Environment (T.M. Church, ed.) (ACS Symposium Series 18, Washington, 1975), pp. 25-55.
- J. Hoigné, B. C. Faust, W. Haag, F. Scully, R. Zepp, In Aquatic Humic Substances (I. H. Suffet, P. McCarthy, eds.) (ACS, Washington, DC, 1989), pp. 363–381.
- 14. N. Baker, L. Wilson, J. Lipid Res., 7, 344 (1966).

1. A. . . .

15. G. R. Harvey, D. A. Boran, L. A. Chesal and J. M. Tokar, Mar. Chem., 12, 119 (1983).