

## Mass transfer phenomena of gaseous hydrocarbons and nitrogen dioxide across gas-inorganic pigments boundaries

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### RÉSUMÉ

La cinétique de la réaction de cinq hydrocarbures (éthane, éthylène, acétylène, propène, boutène) et du dioxyde d'azote avec trois pigments (le blanc de  $\text{TiO}_2$  et les jaunes de  $\text{CdS}$  et  $\text{PbCrO}_4$ ) a été étudiée par chromatographie en phase gazeuse à flux inversé. Le calcul des paramètres cinétiques et des coefficients de transfert de masse a été effectué à partir des isothermes d'adsorption expérimentales en faisant l'hypothèse d'un modèle d'adsorption non-linéaire, qui résulte de la non-uniformité de la surface. Cinq paramètres physico-chimiques ont été obtenus pour chacune des vingt réaction hétérogènes étudiées. A partir de ces résultats obtenus dans des conditions similaires aux conditions atmosphériques, l'extrapolation à des atmosphères réelles paraît possible avec une bonne confiance. Quelques calculs ont été effectués avec un modèle linéaire pour comparaison.

**Mots clés:** réactions d'hydrocarbures avec des pigments et du dioxyde d'azote, chromatographie en phase gazeuse à flux inversé, coefficients de transfert de masse, paramètres cinétiques.

### ABSTRACT

Reversed-flow gas chromatography was used to study the kinetics of the action of five hydrocarbons namely, ethane, ethene, ethyne, propene and butene and of the

nitrogen dioxide, on three known and widely used pigments, the white one  $\text{TiO}_2$ , and the yellows  $\text{CdS}$  and  $\text{PbCrO}_4$ . The calculation of kinetic parameters and mass transfer coefficients is based on an experimental adsorption isotherm. All these calculations are based on a non linear adsorption isotherm model as it is well accepted that the linear one is inadequate for inorganic substances like these mentioned in this work. The inadequacy is mainly attributed to the non-uniformity of the solid surface. Five physicochemical parameters have been obtained for each of the twenty heterogeneous reactions studied. With these systematic experiments under conditions which are similar to the atmospheric ones, an extrapolation of the results obtained to «real» atmospheres with a high degree of confidence is possible. Some of the calculations were based on the linear model for comparison.

**Key words:** Mass transfer phenomena, physicochemical constants, reversed-flow gas chromatography, hydrocarbon-pigments reactions, nitrogen dioxide-pigments reactions

## INTRODUCTION

The surface - coating industry is indeed an ancient one. The origin of paints dates back to prehistoric times. It has been in more recent years, however, that the surface - coating industry has made its greatest strides, which can be attributed to the results of scientific research and the application of modern engineering. Pigments are coloured, organic and inorganic insoluble substances, which are used widely in surface coatings. White lead, zinc oxide and zinc chromate (lithopone) were once the principal white pigments. Today titanium oxide in many varieties is almost the only white pigment used. Coloured pigments consisted among others of lead chromate, and cadmium sulfide. Both of them are yellow [1]. The industrialized society of the 20<sup>th</sup> century, as it is known, has caused a radical change in the conditions of preservation and conservation of monuments, buildings and metallic structures, and the atmospheric pollution associated with industrialization is currently threatening extinction for both cultural heritage and nature itself. General industrial emissions come mainly from evaporation during the storage, transportation and utilization of organic chemicals

Whilst emissions occur from a variety of industries, the petroleum industry is the main industrial source of troposphere volatile hydrocarbons.

The more reactive hydrocarbons are expected to perform a key role in the formation of secondary pollutants in urban areas close to emissions sources. What is really important is the kinetic study of interaction of these hydrocarbons with pigments which consist the coloured basis of different paints of works of art. On the other hand, it is known [2,3] that any heterogeneous reaction between a solid and a gas consists of the following four basic steps:

1. Mass transfer of the gas reactant to the gross exterior surface of the solid material;
2. Diffusional transfer of the gas in and out of the pores of the solid;
3. Adsorption (rather activated) of the gas at the interface; and
4. Possible surface chemical reaction of the adsorbed reactant.

Steps 1-3 can be simplified by considering two overall mass transfer coefficients, one in the gas phase and one in the solid phase. It is their ratio that gives the equilibrium constant for the distribution of the gas between the solid and gaseous phases, according to the linear isotherm model [2,3]. But as mentioned elsewhere [4], the linear model is inexact when treating with inorganic oxides and sulfides. For this inadequacy the nonuniformity of the surface sites is above all the more responsible. For that reason the linear model is abandoned and replaced by the directly measured experimental isotherm [5].

In the present work a physicochemical study of the reactions between each of the three pigments and the six gases is carried out, according to the non-linear model, with a new chromatographic technique known as reversed - flow gas chromatography (RF-GC). Some of the calculations were based on the linear model (which is described in refs 2, 3) for comparison.

## EXPERIMENTAL

The RF-GC technique [6] involves a flow-rate perturbation of the carrier gas which is achieved experimentally simply by using a four- or six- port gas sampling valve and reversing the direction of flow of the carrier gas, usually for a short time interval. If pure carrier gas passes through the sampling column, nothing happens on reversing the flow. If a solute comes out of the diffusion column at  $z=0$  (cf Fig. 1) as the result of its diffusion into the carrier gas, filling the column  $z$  and also running along the sampling column, the flow reversal records the concentration of the solute at the junction of the sampling column with that of the diffusion one, at the moment of the reversal. This concentration recording has the form of extra chromatographic peaks superimposed on the otherwise continuous detector signal.

The experimental arrangement has been described elsewhere [7,8] and corresponds to that of Fig. 1, which is vary different from the one used in the past, [9-10]. The geometrical characteristics of the cells used in the experiments are given in Table I, together with the mass, external porosity and specific surface of the solids.

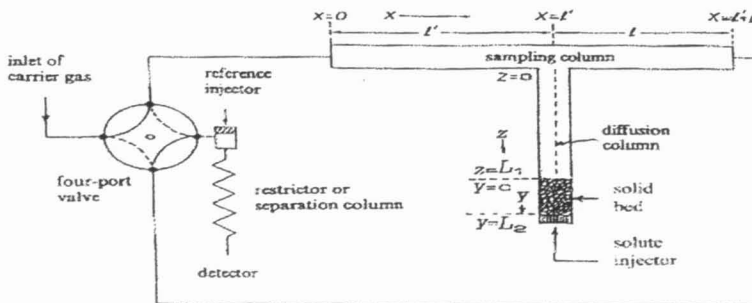


Figure 1 : Schematic representation of the columns and gas connections for the study of mass transfer phenomena. From ref. [8].

All gases used were obtained from Air Liquide (Athens, Greece) and had a purity of 99.000%-99.999%. The solids used were pro-analysi from Merck.

First, the diffusion coefficient of each gas into the nitrogen carrier gas was determined, by using an empty glass vessel. Then, by using the same vessel filled with every solid, the various physicochemical parameters pertaining to the heterogeneous reactions were determined, following the next stages:

- a) Conditioning of each solid *in situ* at 323.2 K for 22 h with nitrogen flowing at the same flow rate.
- b) Injection of 1 cm<sup>3</sup> of each gas at atmospheric pressure.
- c) Measurement of the height of the sample peaks by reversing the direction of the carrier gas flow for 10 s, which is a shorter time than the gas hold-up time.

In all cases the reactant is injected into the diffusion column of Fig. 1 through the solute injector, while the whole cell, comprising the sampling column and the diffusion column, is kept at a constant temperature of 323.2 K inside the chromatographic oven. The carrier gas (pure nitrogen) is running only through the sampling column, filling also the diffusion column, and its direction is reversed from time to time (about 70 double reversals). Each flow reversal creates extra chromatographic peaks, which «sample» the concentration of the reactant at the junction  $x = l'$  of Fig.1. An example of the sample peaks obtained is shown in Fig. 2. The moment of injection is the time 0 and some flow reversals and flow restorations are indicated on the chart recorder strip.

It is the height  $H$  of these peaks (say in cm), measured from the continuous baseline, together with the time  $t$  when the respective flow-reversal was made, that constitute the measurable experimental quantities.

**TABLE I : Lengths and volumes of the cell used to obtain the diffusion bands, together with the solid's amount, external porosity and specific surface area.**

Solid	$L_1/cm$	$L_2/cm$	$V_G/cm$	$V'_G/cm$	$a_s/g\ cm^{-1}$	$\epsilon$	$SSA/cm^2\ g^{-1}$
TiO <sub>2</sub>	21.6	9.6	2.08	0.92	0.07	0.5459	31100
CdS	49.0	5.5	6.15	17.5	4.5	0.7425	25100
PbCrO <sub>4</sub>	49.0	5.5	6.15	17.5	13.63	0.1625	4900

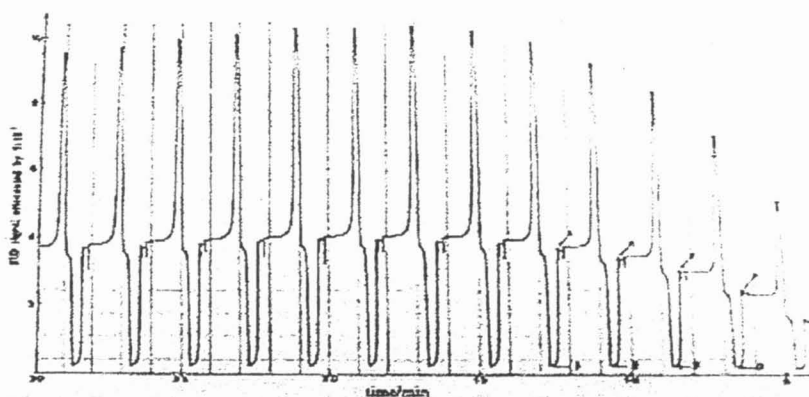


Figure 2 : Sample peaks of propene in nitrogen, in the presence of TiO<sub>2</sub>

## METHOD

The damage measurements for the action of hydrocarbon pollutants on pigments are based on physicochemical quantities. Physicochemical measurements by gas chromatography were performed by creating a diffusion current of the gaseous

solute into the carrier gas, perpendicular to the chromatographic movement, and superimposing on it the effect of a rate or equilibrium process taking place at one end of the diffusion column. Seeking such parameters one has to go through the detailed mechanisms by which the above mentioned pollutants cause the final damage of different works of art. Thus, from a non-distorted diffusion band, the partition coefficient of the gases between a gas phase and a solid phase have been determined, while from a distorted diffusion band, mass transfer and partition coefficients across gas-solid boundaries have been computed, and also adsorption - desorption constants and reaction rate constants when the gas and the solid can react.

The theoretical analysis for the measurement of the desired physicochemical parameters by RF-GC depends on the phenomena being studied and the accuracy adopted.[8,10].

By plotting  $\ln H$  against  $t$ , one obtains the so-called diffusion bands. A typical example is given in Fig. 3. Nothing can be gained by visual examination of such plots, but all physicochemical quantities listed in Tables II-VII are calculated from the diffusion bands, by deriving an equation which describes them mathematically. This was based on the solution of a system of partial differential equations, under given initial and boundary conditions. For this purpose, it is not necessary to determine the isotherm equation separately. Only the basic definition of the local adsorption equation is adopted, thus incorporating the real experimental isotherm in the mathematical calculations. Any possible non-linearity is automatically taken care of. The above definition is

$$c^*_s = \frac{m_s}{a_s} \delta(y - L_2) + k \int_0^t c_y(\tau) d\tau \quad (1)$$

where

$c_s^*$  = equilibrium adsorbed concentration of the analyte at time  $t$  (mol g<sup>-1</sup>)

$m_s$  = initially adsorbed amount of analyte (mol)

$a_s$  = amount of solid adsorbent per unit length of column bed (g cm<sup>-1</sup>)

$y$  = length coordinate along the filled section  $L_2$  (cm)

$\delta(y-L_2)$  = Dirac's delta function describing the initial condition of the bed, when the analyte is introduced as an instantaneous pulse at the point  $y = L_2$  (cm<sup>-1</sup>)

$k$  = equilibrium factor transforming into  $c_s$  the area under the curve of the gaseous concentration  $c_y$  (mol cm<sup>-3</sup>) in region  $L_2$  vs time at any later time  $t$  (cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>)

$c_y$  = gaseous concentration of the analyte as a function of time  $t$  and coordinate  $y$  along the column (mol cm<sup>-3</sup>).

$\tau$  = dummy variable for time.

The mass balance equation in the filled region  $L_2$  of the diffusion column is

$$\frac{\partial c_y}{\partial t} = D_2 \frac{\partial^2 c_y}{\partial y^2} - k_{-1} \frac{a_s}{a_y} (c_s^* - c_s) \quad (2)$$

where  $D_2$  (cm<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of the analyte in section  $L_2$ , corresponding to the temperature  $T_2$  of the solid bed,  $c_s$  the concentration of the adsorbed analyte at time  $t$ ,  $k_{-1}$  the desorption rate constant, and  $a_y$  the cross sectional area of the void space in region  $y$ .

The rate of change of the adsorbed concentration is

$$\frac{\partial c_s}{\partial t} = k_{-1} (c_s^* - c_s) - k_2 c_s \quad (3)$$

the  $k_2$  denoting a possible first-order or pseudofirst-order surface reaction of the adsorbed analyte.

The initial conditions  $c_y(0, y) = \frac{m}{a_y} \delta(y - L_2)$  and  $c_s(0, y) = 0$  where  $m$  is the amount of analyte introduced as a pulse.



An equation analogous to Eq. (2) omitting the last term on the right-hand side, is hold true for the gaseous concentration of the analyte in region  $z$ . In this region the diffusion coefficient is  $D_1(\text{cm}^2 \text{s}^{-1})$ . The system of partial differential equations formed above is solved by using double Laplace transforms of all terms with respect to time and length coordinates, under the given initial conditions and  $c_z(z, 0) = 0$ , the isotherm Eq.(1) and subject to the appropriate boundary conditions at the junctions  $L_2/L_1$  and  $x = l'$  (cf. Fig. 1). By means of certain approximations [6] this leads to the expression

$$H^{l'M} = A_1 \exp(B_1 t) + A_2 \exp(B_2 t) + A_3 \exp(B_3 t) \quad (4)$$

where  $M$  is the response factor of the detector (1 for a F.I.D.),  $g$  is a calibration factor, calculated as described in detail elsewhere [5], and  $c(l', t)$  the concentration of the reactant at  $x = l'$  and time  $t$ . This is the equation describing the diffusion bands (cf. Fig. 3), and the physical meaning of the exponential coefficients of time  $B_1$ ,  $B_2$  and  $B_3$  are as follows:

$$X = \frac{a_1}{1+V_1} + k_{-1} + k_2 = -(B_1 + B_2 + B_3) \quad (5)$$

$$Y = \frac{(k_{-1} + k_2)a_1 + V_1 k_1'}{1+V_1} = B_1 B_2 + B_1 B_3 + B_2 B_3 \quad (6)$$

$$Z = \frac{V_1 k_1' k_2}{1+V_1} = -B_1 B_2 B_3 \quad (7)$$

where

$a_1$  = diffusion parameter of A in the gas phase of region  $z$  equal to  $2D_1/L_1^2$  ( $\text{s}^{-1}$ ),  $D_1$  being the diffusion coefficient of the analyte in the empty region  $L_1$ .

$V_1 = \frac{2V_G'(\text{empty})\varepsilon}{V_G} + \frac{a_1}{a_2}$ , a dimensionless quantity,  $L_1$  and  $L_2$  being the lengths of the section  $z$  and  $y$  of the diffusion column, respectively,  $V_G$  and  $V_G'$  their gaseous

volumes,  $\varepsilon$  the external porosity of the solid bed and  $a_2=2D_2/L_2^2$  ( $D_2$  is the diffusion coefficient of the analyte in section  $L_2$  as it was described above).

By entering the values of the pairs  $H$  (peak height),  $t$  (time of reversal) in the DATA lines 2000-2020 of a PC programme listed in Appendix A of ref.5, the exponential coefficients  $B_1$ ,  $B_2$  and  $B_3$  of Eq. (4) are computed by a non-linear least-squares fitting. From these, using Eqs (5)-(10),  $k_1$ ,  $k_{-1}$  and  $k_2$  are calculated as

$$k_1' = \left[ (1+V_1)Y + \left( \frac{a_1}{1+V_1} - X \right) a_1 \right] / V_1 \quad (8)$$

$$k_{-1} = X - \frac{a_1}{1+V_1} - k_2 \quad (9)$$

$$k_2 = \frac{Z(1+V_1)}{V_1 k_1'} \quad (10)$$

Finally,  $k$  of the isotherm is found from  $k_1$  and  $k_{-1}$  through the Eq. (11) and then, the deposition velocity is calculated by the relation (12):

$$k_1 = k_{-1} k a_s / a_v \quad (s^{-2}) \quad (11)$$

$$V_d = \frac{k}{S} \left( \frac{k_2}{k_{-1} + k_2} \right) \quad (12)$$

where  $S(\text{cm}^2 \text{g}^{-1})$  is the specific surface area of the adsorbent and the reaction probability  $\gamma$  is found by means of the relation (13):

$$\frac{1}{\gamma} = \left[ \frac{R_g T}{2\pi M} \right]^{1/2} / V_d + \frac{1}{2} \quad (13)$$

$R_g$  being the gas constant and  $M$  the molar mass of the analyte.

All these calculations are carried out with the help of a simple PC programme, as mentioned above. Thus, only three original parameters  $k_1$ ,  $k_{-1}$  and  $k_2$  are fitted to the experimental data  $H$ ,  $t$  simultaneously, and from them  $k$ ,  $V_d$  and  $\gamma$  are calculated as derived parameters according to Eqs. (11), (12) and (13), respectively. The exponential stripping method of the PC programme [5], used to calculate the exponential coefficients of time of Eq. (4) is guided by the overall goodness of fit expressed by the square of correlation coefficient  $r^2$ . This coefficient was in the range 0.991-0.999 showing a remarkable goodness of fit for a non-linear regression analysis. The programme [5] also prints, together with the  $B$  values, their standard errors, which were reasonable enough for physicochemical measurements.

## RESULTS AND DISCUSSION

The calculation of the physicochemical parameters, shown in Tables II-VII, by means of the appropriate PC programme of ref.[5], is based on the theoretical analysis developed in the section METHOD. Under  $A$ 's and  $B$ 's of the algebraic sum of the three exponential functions of time, all the corresponding calculated kinetic parameters are hidden.

The diffusion bands obtained, like that of Fig.3, were analyzed in two ways, differing basically in the adsorption isotherm employed. The one uses a linear isotherm approximation [3], while the other [11] takes into account the real experimental isotherm.

In the non-linear isotherm model the gas exchange rates are globally given either as an exchange constant, the deposition velocity  $V_d$  or its reciprocal, which measures the «resistance» of the interface to gas transfer, while the linear one calculates the overall mass transfer coefficients  $K_G$  and  $K_S$ . The specific interaction gas-surface can be represented by using the concept of reaction probability,  $\gamma$ . This coefficient, may take values between 0 (no reaction) and 1 (perfect sink surface). To the above one must add the local equilibrium parameter  $k$  for the adsorption isotherm of the gases studied on the solid pigments, which replaces the equilibrium constant  $K$  (in linear model) for the distribution of the gas between the two phases. Besides, the rate constant of the desorption from the surface  $k_{-1}$  and the rate constant of a possible surface reaction  $k_2$  can be determined as well (the corresponding calculated parameters in the linear model are  $k_1$ ,  $k_{-1}$  and  $k_2$ ). All parameters,  $V_d$ ,  $\gamma$ ,  $k$ ,  $k_{-1}$  and  $k_2$ , that are listed in Tables II-VII can be measured in the same experiment, under non - steady state conditions. All these calculations are based on a non linear adsorption isotherm model.

Some of the calculations were based on the linear model (which is described in refs 2, 3) and are listed in Tables VIII-IX for comparison.

Comparison between the values of  $k_1$  and  $k_{-1}$  (the  $k_1$  multiplied by  $a_y/a_s$ ), also between  $k_{-1}$  (linear) and  $k_{-1}$  (non-linear), as well as between  $K$ 's derived from the ratios  $k_1/k_{-1}$  and  $k/k_{-1}$ , shows that in most cases there is a big difference between the two. For example, in the system  $C_2H_6 / TiO_2$  in Table VIII  $k = 1.04 \times 10^{-4} \times 0.750 = 7.8 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$  and  $k_{-1} = 14.13 \times 10^{-4} \text{ s}^{-1}$ , while in the same system from Table II we get  $k = 86 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$  and  $k_{-1} = 3.23 \times 10^{-3} \text{ s}^{-1}$ , i.e., 11 times bigger  $k$  value and 2.3 times bigger  $k_{-1}$  value. The  $K$  values are found as 0.055 and  $0.27 \text{ cm}^3 \text{ g}^{-1}$ , i.e., 4.8 times bigger in the second case of the experimental isotherm.

Comparing the definition of  $V_d$  by Eq.(12) with that of  $K_G$  as given in ref. 2:

$$K_G = \frac{k_1 V_G'}{A_S} = \frac{k_1 a_y L_2}{S_a a_S L_2} = \left( \frac{k_1 a_y}{a_S} \right) \frac{1}{S_a} = \frac{k}{S_a} \quad (14)$$

where  $A_S$  is the total surface area of the solid, one sees that  $V_d$  is analogous to  $K_G$ , except for the correction factor  $k_2 / (k_1 + k_2)$ , taking care of a possible irreversible surface reaction of the solute. Also,  $k_1 a_y / a_S$  is analogous to  $k$ . The only physicochemical assumptions concerning the gas / solid interactions are that all parameters measured directly or calculated indirectly refer to elementary steps at equilibrium. Based on that, the ratio  $k_1 / k_{-1}$  in the method with the linear isotherm, and  $k / k_{-1}$  in the method with the real experimental isotherm represent equilibrium distribution constants  $K$ , according to the principle of microscopic reversibility.

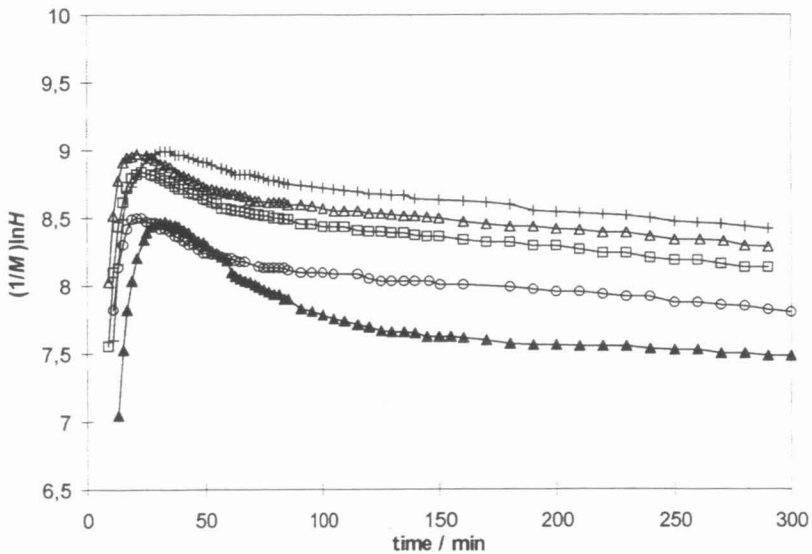


Figure 3 : Diffusion bands obtained with  $1 \text{ cm}^3 \text{ C}_x\text{H}_y$ , injected into a vessel containing CdS, at  $323.2\text{K}$ .  $\text{C}_2\text{H}_2$ ,  $\Delta$   $\text{C}_2\text{H}_4$ ,  $\circ$   $\text{C}_2\text{H}_6$ ,  $\square$   $\text{C}_3\text{H}_6$ , +  $1\text{-C}_4\text{H}_8$   $\blacktriangle$

**TABLE II :** Kinetic parameters and mass transfer coefficients for the Ethane action on the three pigments, i.e. deposition velocities  $V_d$ , reaction probabilities  $\gamma$ , local adsorption parameters of the experimental adsorption isotherm  $k$ , desorption rate constants  $k_1$  and surface reaction rate constants  $k_2$  at 323.2 K, using the non-linear adsorption isotherm model [5,11].

Solid	$10^{10} V_d/\text{cm s}^{-1}$	$10^{14} \gamma$	$10^5 k/\text{cm}^3 \text{ s}^{-1} \text{ g}^{-1}$	$10^3 k_1/\text{s}^{-1}$	$10^5 k_2/\text{s}^{-1}$
TiO <sub>2</sub>	24.7	20.7	86.0	3.23	31.8
CdS	2.37	1.99	67.6	3.11	2.77
PbCrO <sub>4</sub>	2.59	2.17	8.00	2.65	4.28

**TABLE III :** Kinetic parameters and mass transfer coefficients for the Ethene action on the three pigments, i.e. deposition velocities  $V_d$ , reaction probabilities  $\gamma$ , local adsorption parameter of the experimental adsorption isotherm  $k$ , desorption rate constants  $k_1$  and surface reaction rate constants  $k_2$  at 323.2 K, using the non-linear adsorption isotherm model [5,11].

Solid	$10^{10} V_d/\text{cm s}^{-1}$	$10^{14} \gamma$	$10^5 k/\text{cm}^3 \text{ s}^{-1} \text{ g}^{-1}$	$10^3 k_1/\text{s}^{-1}$	$10^5 k_2/\text{s}^{-1}$
TiO <sub>2</sub>	54.2	43.9	312	6.02	34.3
CdS	2.15	1.74	78.3	3.39	2.35
PbCrO <sub>4</sub>	2.90	2.35	8.75	2.98	4.92

**TABLE IV :** Kinetic parameters and mass transfer coefficients for the Ethyne action on the three pigments, i.e. deposition velocities  $V_d$ , reaction probabilities  $\gamma$ , local adsorption parameters of the experimental adsorption isotherm  $k$ , desorption rate constants  $k_1$  and surface reaction rate constants  $k_2$  at 323.2 K, using the non-linear adsorption isotherm model [5,11].

Solid	$10^{10} V_d/\text{cm s}^{-1}$	$10^{14} \gamma$	$10^5 k/\text{cm}^3 \text{ s}^{-1} \text{ g}^{-1}$	$10^3 k_1/\text{s}^{-1}$	$10^5 k_2/\text{s}^{-1}$
TiO <sub>2</sub>	49.7	38.7	177	3.90	37.3
CdS	1.99	1.55	74.5	3.82	2.58
PbCrO <sub>4</sub>	2.08	1.62	8.13	4.02	5.11

**TABLE V :** Kinetic parameters and mass transfer coefficients for the Propene action on the three pigments, i.e. deposition velocities  $V_d$ , reaction probabilities  $\gamma$ , local adsorption parameters of the experimental adsorption isotherm  $k$ , desorption rate constants  $k_{-1}$  and surface reaction rate constants  $k_2$  at 323.2 K, using the non-linear adsorption isotherm model [5,11].

Solid	$10^{10} V_d/\text{cm s}^{-1}$	$10^{14} \gamma$	$10^5 k/\text{cm}^3 \text{ s}^{-1} \text{ g}^{-1}$	$10^3 k_{-1}/\text{s}^{-1}$	$10^5 k_2/\text{s}^{-1}$
TiO <sub>2</sub>	38.2	37.8	154	2.83	23.7
CdS	2.45	2.43	59.5	2.55	2.67
PbCrO <sub>4</sub>	2.17	2.16	7.55	2.83	4.05

**TABLE VI :** Kinetic parameters and mass transfer coefficients for the 1-butene action on the three pigments, i.e. deposition velocities  $V_d$ , reaction probabilities  $\gamma$ , local adsorption parameters of the experimental adsorption isotherm  $k$ , desorption rate constants  $k_{-1}$  and surface reaction rate constants  $k_2$  at 323.2 K, using the non-linear adsorption isotherm model [5,11].

Solid	$10^{10} V_d/\text{cm s}^{-1}$	$10^{14} \gamma$	$10^4 k/\text{cm}^3 \text{ s}^{-1} \text{ g}^{-1}$	$10^3 k_{-1}/\text{s}^{-1}$	$10^5 k_2/\text{s}^{-1}$
TiO <sub>2</sub>	23.0	26.4	10.3	2.13	16.0
CdS	1.40	1.60	4.47	2.03	1.61
PbCrO <sub>4</sub>	1.76	2.02	1.58	5.30	2.91

**TABLE VII :** Kinetic parameters and mass transfer coefficients for the nitrogen dioxide action on the three pigments, i.e. deposition velocities  $V_d$ , reaction probabilities  $\gamma$ , local adsorption parameters of the experimental adsorption isotherm  $k$ , desorption rate constants  $k_{-1}$  and surface reaction rate constants  $k_2$  at 323.2 K, using the non-linear adsorption isotherm model [5,11].

Solid	$10^{10} V_d/\text{cm s}^{-1}$	$10^{14} \gamma$	$10^4 k/\text{cm}^3 \text{ s}^{-1} \text{ g}^{-1}$	$10^4 k_{-1}/\text{s}^{-1}$	$10^4 k_2/\text{s}^{-1}$
TiO <sub>2</sub>	25.0	25.7	3.65	28.97	7.76
CdS	6.6	6.8	2.65	96.73	6.40
PbCrO <sub>4</sub>	17.3	18.0	-0.17	0.32	-

**TABLE VIII :** Kinetic parameters and mass transfer coefficients for the hydrocarbons action on the  $TiO_2$  pigment, i.e. the mass transfer coefficients in the gas  $K_G$  and in the solid  $K_S$ , the adsorption equilibrium constants  $K$ , the adsorption rate constants  $k_1$  and the desorption ones  $k_{-1}$ , as well as the surface reaction rate constants  $k_2$ , at  $T = 323.2$  K, using the linear adsorption isotherm model [2].

$C_XH_Y$	$10^4 k_1/s^{-1}$	$10^4 k_{-1}/s^{-1}$	$10^5 k_2/s^{-1}$	$10^5 K_G/cm s^{-1}$	$10^4 K_S/cm s^{-1} K$	
$C_2H_2$	1.14	7.60	3.23	6.83	1.54	0.18
$C_2H_4$	71.95	7.50	33.28	432.03	1.52	11.53
$C_2H_6$	1.04	14.13	33.27	62.08	2.87	0.88
$C_3H_6$	1.04	6.00	3.57	6.22	1.22	0.21
$1-C_4H_8$	1.26	5.32	3.59	7.54	1.08	0.28

**TABLE IX :** Kinetic parameters and mass transfer coefficients for the hydrocarbons action on the CdS pigment, that is the mass transfer coefficients in the gas  $K_G$  and in the solid  $K_S$ , the adsorption equilibrium constants  $K$ , the adsorption rate constants  $k_1$  and the desorption ones  $k_{-1}$ , as well as the surface reaction rate constants  $k_2$ , at  $T = 323.2$  K, using the linear adsorption isotherm model [2].

$C_XH_Y$	$10^4 k_1/s^{-1}$	$10^4 k_{-1}/s^{-1}$	$10^5 k_2/s^{-1}$	$10^{10} K_G/cm s^{-1}$	$10^{11} K_S/cm s^{-1} K$	
$C_2H_2$	6.43	3.89	1.56	2.46	4.14	5.95
$C_2H_4$	7.40	3.65	1.60	2.84	3.89	7.30
$C_2H_6$	5.60	3.54	2.24	2.15	3.77	5.70
$C_3H_6$	4.59	3.47	2.10	1.76	3.69	4.77
$1-C_4H_8$	5.33	1.05	0.86	2.04	1.11	18.33

From all these physicochemical quantities measured under the same experimental conditions, it is obvious a much more different behaviour of the three pigments as well as of the six gaseous reactants. This is justified by the different chemical compositions



of them. Among the solids,  $\text{TiO}_2$  seems to be the most reactive and CdS the less. Among the hydrocarbons, the unsaturated ones are more reactive than the saturated ethane, and the hydrocarbons with the lower molecular weight exhibit the highest reactivity. Nitrogen dioxide on the other hand has a significant attack by itself and it is possible by means of RF-GC technique to measure precisely its recognized attack.

Thus, by means of the constants  $k_1, k_{-1}$  the reversible phenomena of adsorption - desorption, taking place in the gas -solid boundaries, are studied in a quantitative level (order of magnitude  $10^{-3}$ ), while through the  $k_2$  (order of magnitude  $10^{-5}$ ), any irreversible phenomenon can be investigated.

Contrarily to other techniques, either chromatographic or not, which take the adsorption phenomena as negligible, all  $k_{-1}$  values provided by this one lead to more realistic models and mechanisms. Moreover, the mass transfer coefficients related directly to the adsorption-desorption phenomena provide a steady scientific basis for kinetic data interpretation.

Finally, the experimental data concerning diffusion coefficients, rate constants etc are in good agreement with the results obtained by other groups with the same or other techniques (refs. 10, 12-17).

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## REFERENCES

- 1 Norris Shreve R., Brink Jr J.A. (1977) *Chemical Process Industries*. Mc Graw-Hill Kogakusha, L.T.D., fourth edition, London, p. 380.
- 2 Katsanos N.A., Agathonos P., Niotis A. (1988) Mass transfer phenomena studied by reversed-flow gas chromatography. 2. Mass transfer and partition coefficients across gas-solid boundaries. *J Phys Chem* 92, 1645-1650.
- 3 Vassilakos Ch., Katsanos N.A., Niotis A. (1992) Physicochemical damage parameters for the action of SO<sub>2</sub> and NO<sub>2</sub> on single pieces of marble. *Athmos Environ* 26A, 219- 223.
- 4 Gates B. (1992) *Catalytic Chemistry*. John Wiley and sons Inc., New York, p. 327.
- 5 Sotiropoulou V., Vassilev G.P., Katsanos N.A., Metaxa H., Roubani-Kalantzopoulou F. (1995) Simple determination of experimental isotherms by diffusion denuder tubes. *J Chem Soc Faraday Trans* 91, 485- 492.
- 6 Katsanos N.A. (1988) *Flow Perturbation Gas Chromatography*. Marcel Dekker, New York, 87, 113, p. 163.
- 7 Zahariou-Rakanta H., Kalantzopoulos A., Roubani-Kalantzopoulou F. (1997) Chromatographic study of the influence of nitrogen dioxide on the reactions between volatile hydrocarbons and inorganic pigments. *J Chromatogr A* 776, 275-282.
- 8 Abatzoglou Ch., Iliopoulou E., Katsanos N.A., Roubani-Kalantzopoulou F., Kalantzopoulos A. (1997) Deposition parameters of air pollutants on solid surfaces, measured in the presence of surface and gaseous reactions, with a simultaneous determination of the experimental isotherms. *J Chromatogr A* 776, 211-224.
- 9 Katsanos N.A., Roubani-Kalantzopoulou F. (1995) Denuder tubes used with gas chromatographic instrumentation to measure rate coefficients and equilibrium constants. *J Chromatogr A* 710, 191-228.
- 10 Karagiorgos G., Roubani-Kalantzopoulou F. (1998) A kinetic study of homogeneous and heterogeneous reactions of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and O<sub>3</sub>. *Z Phys Chem* 203, 231-246.
- 11 Katsanos N.A., Sotiropoulou V., Roubani-Kalantzopoulou F., Metaxa H. (1995) Measurement of deposition velocities and reaction probabilities of air pollutants with solid surfaces, in the presence of gas-phase chemical reactions and non-linear adsorption isotherms. *Analytical Laboratory*, 5, 13-17.
- 12 Xinqin Yun, Zobo Long, Dengmin Kou, Xianyu, Lu, Hexuan Li (1995) Determination of adsorption equilibrium constants by reversed-flow gas chromatography. *J Chromatogr A*, 736, 151-156.
- 13 Katsanos N.A., Karaiskakis G. (1982) Measurement of diffusion coefficients by reversed-flow gas chromatography instrumentation. *J Chromatogr* , 237, 1-14.

- 14 Katsanos N.A., Karaiskakis G. (1983) Temperature variation of gas diffusion coefficients measured by the reversed-flow sampling technique. *J Chromatogr*, 254, 15-25.
- 15 Henriksen J.F. (1995) Reaction of gases on calcareous stones under dry conditions in field and laboratory studies. *Water, Air and Soil Pollution*, 85, 2707-2712.
- 16 Roubani-Kalantzopoulou F., Kalogirou E., Kalantzopoulos A., Metaxa H., Thede R., Katsanos N.A., Sotiropoulou V. (1997) A differential method for the analysis of chemical kinetics results based on reversed-flow gas chromatography. *Chromatographia*, 46, 161-169.
- 17 Kalantzopoulos A., Abatzoglou Ch., Roubani-Kalantzopoulou F. (1997) *Interfaces Against Pollution*, Wageningen, The Netherlands, August p. 122 Environmental Catalysis studied by the Reversed-Flow Gas Chromatography. Measurements, Mechanism and Models *Colloids and Surface A*, accepted for publication.