Surface Prechlorination of Anatase TiO_2 for Enhanced Photocatalytic Oxidation of Toluene and Hexane

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

We report the influence of prechlorination of TiO_2 powder on the activity for the photocatalyzed oxidation of hydrocarbons (toluene, hexane) and oxygenates (acetone, butan-1-ol). Water- and HCl-pretreated catalyst are prepared by impregnation of TiO_2 powder in H_2O and in HCl solutions, respectively, followed by drying at room temperature. X-Ray photoelectron spectroscopy (XPS) analysis demonstrates the surface prechlorination efficiency: 1 g of TiO_2 impregnated with 3 ml of 3N HCl solution results in a chlorine surface concentration of 1.6%. Prechlorination results in a photo-oxidation-rate enhancement for toluene and hexane, no change for butan-1-ol, and inhibition for acetone. This pattern is the same as that demonstrated earlier by us when these reactants are co-fed with the chlorine source trichloroethylene (TCE).

Introduction. – *Berman* and *Dong* [1] first reported that the presence of trichloroethylene (TCE) brought about a photocatalytic rate enhancement for the rate of conversion of three air contaminants, 2-methylheptane, CH_2Cl_2, and $CHCl_3$. *Luo* and *Ollis* [2], and *Sauer et al.* [3] successfully demonstrated photocatalyzed rate enhancement for the aromatic toluene when co-fed with any of the three chloro-olefins TCE, perchloroethylene, or trichloropropene. *d' Hennezel* and *Ollis* [4] broadened this field with a study of 18 compounds to test their susceptibility to rate enhancement *via* co-feeding of the chloro-olefin TCE. The mechanism of this enhancement is not confirmed, but appears likely to be associated with the Cl radicals produced during the very fast conversion of chloro-olefins, some of the most reactive compounds studied in photocatalysis. A surface chain-reaction mechanism involving $Cl^{\bullet}$ in the propagation sequence has been previously suggested by *Nimlos et al.* for TCE in air conversions [5]; we have subsequently suggested that our enhancement, when present, is due to a chain-transfer mechanism involving $Cl^{\bullet}$ [2][6].

The co-feeding method for enhancing the photoefficiency of conversion of an air pollutant has some appeal, but has two major process drawbacks: *a*) TCE itself is a hazardous compound, so industrial users will be reluctant to add it to an air stream to carry out decontamination and, *b*) certain pollutants, especially oxygenates, bind strongly to the TiO_2 surface, displacing the more weakly bound TCE so that it is not appreciably degraded, and consequently no Cl-based rate enhancement is observed.

This paper demonstrates that an alternative approach, that of prechlorination of the titania surface, leads to the same pattern of rate enhancement, indifference, or inhibition as found for co-feeding TCE and a particular reactant. Such pretreatment, where advantageous, allows a boost in catalyst activity without need to add a Cl source to the feedstream.

Experimental. – *Sample Preparation.* Untreated TiO_2 powder (*Degussa P25 TiO_2*) catalyst was characterized by the manufacturer as having a primary particle diameter of 21 nm, a surface area of 50 m^2/g, and a crystal structure of mostly anatase. The particles were spherical and nonporous, with stated purity of > 99.5% TiO_2. Stated impurities included Al_2O_3 (< 0.3%), HCl (< 0.3%), SiO_2 (< 0.2%), and Fe_2O_3 (< 0.01%). This catalyst was used as supplied, without pretreatment.

TiO_2 was impregnated with H_2O (TiO_2/H_2O) by mixing 1 g of TiO_2 with 3 ml of deionized H_2O; this preparation was allowed to dry in a desiccator at r.t. before grinding. This H_2O-pretreated TiO_2 sample was kept in the desiccator for storage, and aliquots were used when needed.

Photocatalytic Reaction. The photocatalyzed oxidative degradations of toluene, hexane, butan-1-ol, acetone, and TCE were carried out with near-UV illuminated TiO_2 powder (anatase) in a flow reactor (described previously [2][3][7]). The model contaminants toluene and hexane were of HPLC grade, and the acetone of certified grade, all supplied by *Fisher*. The butan-1-ol used was of HPLC grade, and the TCE was above 99% purity, both from *Aldrich*. The pressurized gases (air, He, H_2) were scientific grade, supplied by a local vendor. A 100 W black-light lamp provided vertical, near-UV illumination at 300–400 nm. All experiments were performed at 22–24°. The air-flow rate (FR) was set at 0.82 (FR1), 0.74 (FR2), or 3 (FR3) cm^3/min. The relative humidity was maintained at 70% (1000 mg H_2O/m^3). The mass of TiO_2 used was 25 mg for TiO_2, and 50 mg for TiO_2/H_2O, and TiO_2/HCl; these amounts ensured, in each case, an optical density > 2, *i.e.*, complete opacity of the catalyst layer to the incident light.

X-Ray Photoelectron Spectroscopy (XPS). X-Ray photoelectron spectra were acquired with a *Physical Electronics PHE-5400* system. The source was a *MG alpha* anode (1253.6 eV), operating at 400 W, 15 kV. The system pressure during analysis was $3-4 \times 10^{-9}$ Torr. Before XPS, each sample was compressed on an In foil.

Results. – *XPS. Fig. 1,a–c* presents the Ti (2p1/2, 3/2), O (1s), and C (1s) X-ray photoelectron spectra, respectively, for untreated TiO_2, and *Fig. 1,d* shows a juxtaposition of the Cl (2p) spectra for the three TiO_2 samples. These are the only four elements detected on our sample surfaces. For TiO_2/H_2O, and TiO_2/HCl photocatalysts, the spectra for Ti, O, and C were identical in shape to those of *Fig. 1,a–c*, and also to spectra previously reported for a TiO_2 standard [8][9].

The C (1s) signal shows a surface charging of 1.5–1.9 eV; the binding energies shown in *Fig. 1* are not charge-corrected. Instead, we calculated the binding-energy difference (ΔE_B) between the O (1s) and Ti (2p3/2). This value is a reliable indicator of the Ti oxidation state [8][9], as it permits discrimination among the 2^+, 3^+, and 4^+ oxidation states of Ti. The ΔE_B for our three samples is 71.1 ± 0.1 eV, indicative of Ti in the 4^+ oxidation state [8–10]. The C (1s) spectra of all three powders indicates three components (a deconvolution is shown in *Fig. 1,c*). The main C (1s) band at 284.5 eV corresponds to simple hydrocarbons (C–C and C–H). The next higher binding-energy component (286.1 eV) is probably C–O (*e.g.*, alcohol or ether). The highest binding-energy (288.8 eV) component is likely to be a carboxyl C-atom (O–C=O). The above binding energies of carbon are the experimental values corrected by 1.5 eV for surface charging. Each binding-energy value falls into the appropriate carbon-type binding-energy range given in [11].

The full width at half maximum of the Ti (2p3/2) peak is equal to 1.4 eV, consistent with that for pressed TiO_2 powders [9].

Ca. 14–17% of the total oxygen peak (*Fig. 1,b*) exhibits a lower binding energy, corresponding to H_2O or OH groups on the surface of the samples.

The Cl peak (*Fig. 1,d*) is a *doublet* separated by 1.6 eV; the curve fit suggests only one chloride component of binding energy 199.7 eV ($199.7 - 1.5 = 198.2$ eV, charge corrected), which is most likely alkaline Cl, the logical replacement of alkaline OH surface groups. An organic Cl component would have a binding energy of *ca.* 200 eV(11) (201.5, with surface charging). *Fig. 1,d* shows clearly increasing Cl levels for

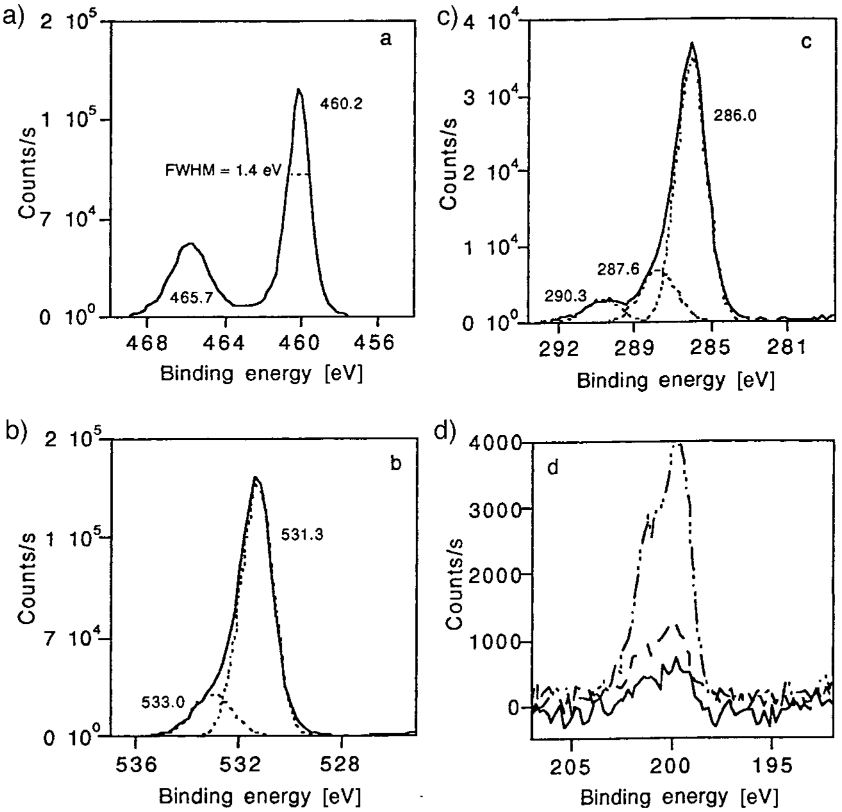

Fig. 1. *XPS from fresh untreated TiO_2 (Degussa P25) of* a) *Ti (2p),* b) *O (1s),* c) *C (1s), and* d) *for untreated TiO_2 (——), TiO_2/H_2O (----), TiO_2/HCl (----) for Cl (2p)*

the TiO_2, TiO_2/H_2O, and TiO_2/HCl samples, respectively. The *Table* gives the relative atomic abundances of the four elements found on the surface of the three samples, determined by normalization of the integrated areas of each photo-peak with its elemental sensitivity factor provided in [11].

Table. *Relative Atomic Abundances* [%] *of Pretreated TiO_2*

	Ti (2p)	C (1s)	O (1s)	Cl (2p)
TiO_2	19.6	30.7	49.4	0.2
TiO_2/H_2O	23.8	18.8	57.0	0.4
TiO_2/HCl	21.6	28.3	48.5	1.6

Photocatalytic Data. Fig. 2 presents the oxidation of toluene as a function of time for different TiO_2 samples. The lowest conversion is realized for toluene in air flowing over an untreated TiO_2 sample. The conversion *vs.* time is only slightly better for the TiO_2/H_2O samples. In both cases, within 3 min of reaction, the conversion drops quickly from the initial 75–80% due to apparent catalyst deactivation. However, when Cl is

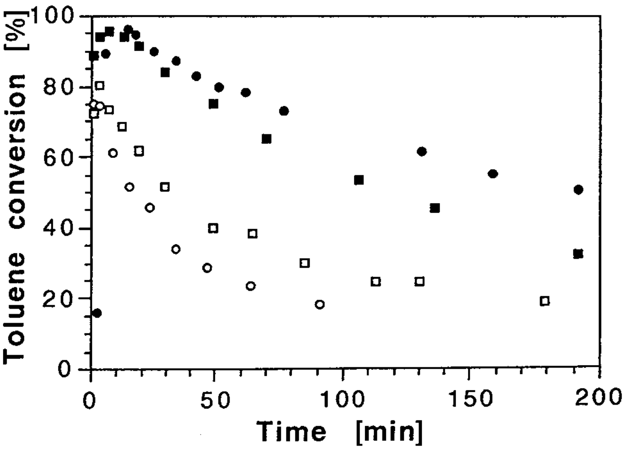

Fig. 2. *Toluene oxidation as a function of time.* Toluene initially at 50 (±2) mg/m^3 and H_2O at 1000 mg/m^3; TiO_2, flow rate 0.74 cm^3/s (○); TiO_2/H_2O, flow rate 0.74 cm^3/s (□); TiO_2/HCl, flow rate 0.74 cm^3/s (■); TiO_2, flow rate 0.82 cm^3/s, TCE initially at 290 mg/m^3 (●).

present on the catalyst surface, either from simultaneous TCE destruction in a mixed toluene/TCE air feed or from the HCl pretreatment, the initial conversion is not only increased to >95% but is maintained at >90% for 20 min. Catalyst deactivation is also delayed substantially when surface Cl is present.

For the saturated reactant hexane (*Fig. 3*), the lowest conversion (67–77%) is again found with untreated TiO_2 or for TiO_2 treated with H_2O. Adding surface Cl enhances the rate: the conversion is raised to 81% over TiO_2 in the simultaneous presence of TCE, and to 94% over the TiO_2/HCl pretreated sample. As also observed for toluene conversions, the enhancement appears immediately over TiO_2/HCl, whereas several minutes are required to reach maximum conversion when TCE is

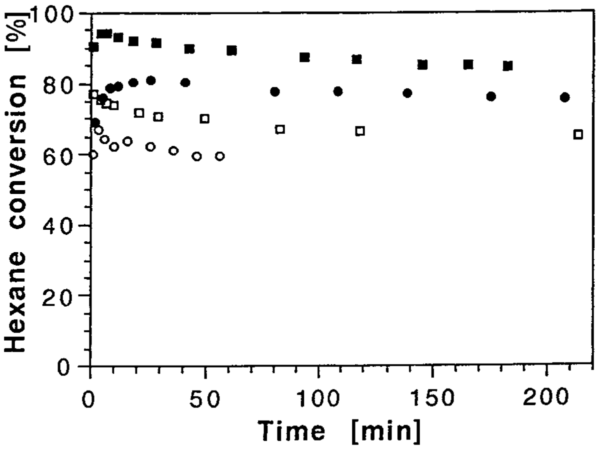

Fig. 3. *Hexane oxidation as a function of time.* Hexane initially at 50 (±2) mg/m^3 and H_2O at 1000 mg/m^3; TiO_2, flow rate 0.74 cm^3/s (○); TiO_2/H_2O, flow rate 0.74 cm^3/s (□); TiO_2/HCl, flow rate 0.74 cm^3/s (■); TiO_2, flow rate 0.82 cm^3/s, TCE initially at 290 mg/m^3 (●).

added to the stream. This difference is consistent with our claim [2–4][6] that the enhancement effect is due to surface Cl radicals: the HCl pretreatment could produce these radicals rapidly from pre-adsorbed Cl^-, whereas the TCE reaction will require some reaction time to accumulate a useful surface Cl level.

The enhancement effect arising from HCl pretreatment is also demonstrated to last over time: the hexane conversion over TiO_2/HCl is greater that that over TiO_2/H_2O for the entire reaction time (>2 h).

For experiments with the strongly adsorbing butan-1-ol, both the air flow rate and the inlet butanol concentration were increased in order to obtain conversions below 100%. For butan-1-ol over TiO_2, no enhancement was observed in the presence of TCE, probably due to the low TCE conversion (17%) and thus low $Cl^•$ production under these conditions [4]. No enhancement is measured here over TiO_2/HCl compared to TiO_2/H_2O (*Fig. 4*); instead, surface prechlorination leads to inhibition of the rate.

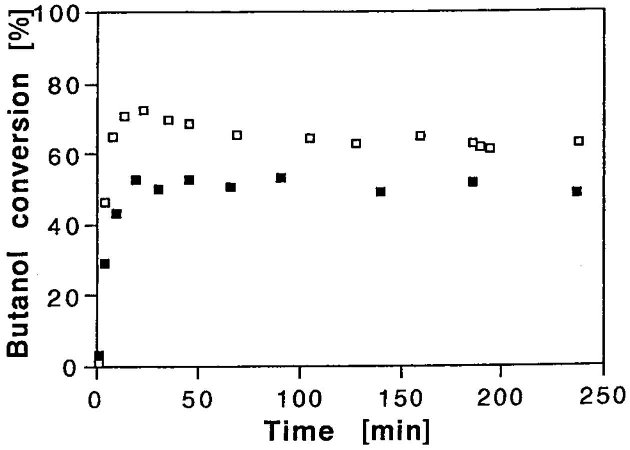

Fig. 4. *Butan-1-ol oxidation as a function of time.* Butan-1-ol initially at 150 (±2) mg/m^3 and H_2O at 1000 mg/m^3; flow rate 3 cm^3/s, TiO_2/H_2O (□) and TiO_2/HCl (■).

For acetone, a weakly bound reactant, our previous finding indicated inhibition of the reaction rate when TCE is present in the feed. Similar inhibition results are observed (*Fig. 5*) when the catalyst is pretreated with HCl *vs.* a simple H_2O pretreatment.

Discussion. – *XPS.* The maximum surface chlorination of anatase TiO_2 before bulk lattice attack is estimated at 6–7 Cl/nm^2 [12–14]. *Munuera et al.* [13] showed experimentally that chlorination of TiO_2 surfaces by reaction with gaseous CCl_4 occurs in two stages. They explained that 5.7 O_2^-/nm^2 with an uncompensated negative charge are distributed into three different levels on a 111 anatase plane, assuming that chlorination occurs according to the reaction:

$$CCl_4(g) + 2\,O^{2-}_{latt} \rightarrow 4\,Cl^-_{surf} + CO_2 \qquad (1)$$

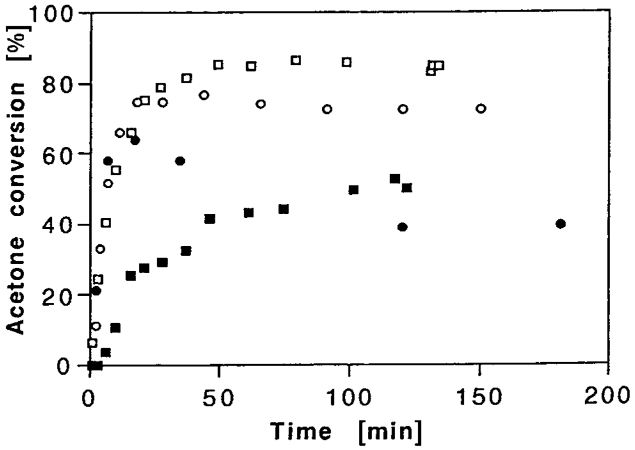

Fig. 5. *Acetone oxidation as a function of time.* Acetone initially at 50 (±2) mg/m^3 and H_2O at 1000 mg/m^3; TiO_2, flow rate 0.74 cm^3/s (○); TiO_2/H_2O, flow rate 0.74 cm^3/s (□); TiO_2/HCl, flow rate 0.74 cm^3/s (■); TiO_2, flow rate 0.82 cm^3/s, TCE initially at 290 mg/m^3 (●).

In the first stage, at 25°, 1.9 lattice O_2^-/nm^2 (first level of uncompensated negative charges) are replaced by 3.8 Cl^-/nm^2. In a second stage (50°), O^{2-} ions of the second level of uncompensated negative charges are removed by the reaction above to yield a fully chlorinated surface with 7 Cl/nm^2. Further chlorination requires exchange of deeper-lying O^{2-} ions and simultaneous loss of $TiCl_4$. Therefore, at room temperature, a maximum surface coverage of 3.8 Cl^-/nm^2 was attained.

Our XPS results give a Cl content of 1.6%. If we assume from earlier work by *Munuera et al.* [13] and *Boehm* [15] that about one-third of all OH groups are exchangeable, we can estimate the expected signal strength. The mean free escape path of XPS electrons is around 10 Å [16] and since the Ti−O bond length is about 2 Å [17], we assume our XPS results are representative of five atomic layers. Each of the five layers is composed of four O-atoms per two Ti-atoms (corresponding to a total XPS signal of $4+2$ elements × 5 layers $=30$ elements) for only two OH groups on the surface of which one-third will exchange for Cl (2(OH)) × 1.3 (exchangeable)/32 (total elements) × 100% $=2.1$%, which is of the same order as our experimental value of 1.6%; the surface carbon is not taken into account as we do not know how it is bound to the surface.

The Cl on the TiO_2/HCl photocatalyst is in a single chemical environment; it shows a *doublet* created by spin-orbit coupling rather the two forms of surface Cl. *Larson* and *Falconer* [10] followed chlorine content on *Degussa P25* TiO_2 before and after its use in the gas-phase photo-oxidation of TCE. No Cl was detected on the fresh sample, whereas the used one exhibited two Cl (2p) peaks separated by 3.1 eV. They suggested that Cl is either part of an adsorbate with Cl bound to different functional groups or adsorbed at two different sites. The total Cl concentration was estimated at 5%. In our opinion, one peak corresponds to adsorbed TCE or chlorinated intermediates, and the other one to Cl bound to Ti. This view is consistent with our hypothesis that TCE degradation chlorinates the TiO_2 surface and is responsible for the observed rate enhancement. *Fig. 1,d* demonstrates that prechlorinating the TiO_2 surface results in one Cl (2p) peak, the same Cl bound to Ti found by *Larson* and *Falconer* [10] for TCE. Addition or prechlorination, therefore, results eventually in a similar, Cl-containing TiO_2 surface, and we demonstrate a comparable photo-oxidation rate enhancement (*Figs. 1* and *2*) or inhibition (*Figs. 3* and *4*).

Photocatalytic Reactions. The conversion of both toluene and hexane is greater over TiO_2/HCl than TiO_2/H_2O for the entire 3 h run. The Cl enhancement is thus demonstrated to last, and both the initial and prolonged enhancement can be rationalized by the mechanism in the *Scheme.*

Scheme

$$\mathrm{Ti{-}Cl^- + H^+ \rightarrow Ti{-}Cl^\bullet}$$

$$\mathrm{Cl^\bullet + P \rightarrow P^\bullet + HCl(g)}\ ^{a})$$

$$\mathrm{P^\bullet + O_2 \rightarrow \ldots \rightarrow CO_2}\ ^{b})$$

$$\mathrm{Ti + H_2O \rightarrow Ti{-}OH + H(ads)}\ ^{c})$$

$$\mathrm{Ti{-}OH + HCl(g) \rightarrow Ti{-}Cl + H_2O}\ ^{d})$$

a) This reaction is faster than the corresponding reaction with $OH^\bullet$ since the gas-phase second-order rate constant is greater ($k_{Cl} > k_{OH}$); there is also a possible reduction of undesirable electron/hole recombination. b) Dark chain-oxidation mechanism; no intermediates are detected by GC/FIC analysis. c) The continuous air stream contains 7% H_2O. d) As described in the *Introduction*, re/surface chlorination.

Rate enhancement by TiO_2 prechlorination might have been attributed to an acid treatment, which could clean the surface by carbon removal. However, illumination pretreatment showed that any initial surface carbon does not influence the photoreaction. Also, the acid treatment could change the crystalline phase or surface area of TiO_2 and, thus, the TiO_2 reactivity. However, *Shastri et al.* [14] showed that TiO_2 soaked in aqueous HCl (3.3% Cl) has a smaller surface area than a TiO_2 sample soaked in distilled H_2O (80 m^2/g instead of 110 m^2/g) after a thermal pretreatment at 100°. Enhancement is, thus, not due to a larger surface area.

The rate enhancement or inhibition trends observed with Cl from TCE addition are identical to those found here over a prechlorinated TiO_2 sample. Toluene and hexane conversions were both enhanced over TiO_2/HCl just as they were in the presence of TCE (*Figs. 1* and *2*, and [2]), this enhancement can be rationalized by the same Cl role propose by *Luo* and *Ollis* [2] and by the mechanism in the *Scheme.* The acetone conversion is inhibited in the presence of TCE as well as by the prechlorination treatment. One possible explanation is that acetone contains only alpha C-atoms, from which hydrogens are harder to abstract (the second-order gas phase chlorine rate constant is one order of magnitude smaller than for other enhanced pollutants). Butan-1-ol conversion was unchanged by the addition of TCE at a flow rate of 3 ml/s. We have postulated [4] that, since TCE degradation reached a maximum conversion of only 17%

in the pesence of butanol, few Cl radicals were produced and little or no rate enhancement of butanol conversion was possible.

Summary. – We have demonstated that a simple prechlorination by HCl impregnation is as efficient as TCE feed addition to raise the photoefficiency of toluene and hexane conversion in photocatalysis. This finding suggests that all pollutants previously found susceptible to TCE rate enhancement *via* TCE co-feeding will also exhibit rate enhancement though TiO_2 photocatalyst prechlorination.

However, we confirm that surface prechlorination does not have a positive effect on either acetone, which contains only α-hydrogens, or strongly adsorbing compounds such as butan-1-ol. This behavior again reflects that observed when co-feeding these compounds with TCE.

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