JOURNAL OF CATALYSIS 66, 383–390 (1980)

Is Photocatalysis Catalytic?

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Received December 26, 1979; revised June 13, 1980

INTRODUCTION

The phenomenon of heterogeneous photocatalysis is probably most often observed in the oxidation of exterior older house paints, a process in which titanium dioxide particles in the paint use part of the sun's energy to oxidize the organic components of the film. (This deterioration is now minimized by coating these semiconductor particles with a thin layer of a more photoinactive oxide such as alumina.) Recent literature reports suggest that certain illuminated semiconductor oxides are "photocatalysts," or more precisely "photoassisted catalysts" (*1*), for more desirable reactions than paint degradation. At ambient conditions, such diverse reactions have been reported as alkane partial oxidation, hydrogen or ammonia production, waste organic acid and cyanide conversion, and chlorinated hydrocarbon decomposition (Table 1). Such versatility for chemical and fuel production, chemical energy storage, BOD reduction, and specific effluent detoxification is intriguing, and suggests a bright future for photon-driven reactions involving solids.

Evaluation of commercial potential requires, among other things, knowledge of catalyst activity and lifetime under expected reaction conditions. *The small quantities of product which typify many initial reports of novel "photocatalytic" reactions lead naturally to these central questions:*

Has the reaction been demonstrated to be catalytic, or is the surface/near-subsurface of the nonstoichiometric semiconductors merely a photoactivated reagent?

How is the fundamental activity of different truly catalytic materials to be compared, i.e., can we calculate the reaction rate per unit surface area from the data reported?

Concerning the first question, the claimed catalytic nature of the photoassisted reduction of nitrogen and decomposition of water has been challenged by van Damme and Hall (*2*). Here we extend that discussion to other reactions observed in the presence of illuminated semiconducting oxides. Informed response to these questions requires consideration of the photon–solid interaction, the basis for specific rate calculations, and the evidence for catalysis.

PHOTOACTIVATION

Absorption of a photon by semiconducting solids (Fig. 1) excites an electron from the valence to the conduction band if the photon energy, $h\nu$, equals or exceeds the semiconductor band gap energy, E_g.

$$h\nu + \text{solid} \rightarrow h^+ + e^-. \qquad (1)$$

Ultraviolet or near-ultraviolet photons are typically required. For an n-type semiconductor, the potential variation across the space-charge region of the solid causes the resulting hole to migrate toward the surface. At steady state, electroneutrality of the surface requires that the arrival rate of both holes and electrons be equal.

Reaction at the surface involves a series

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0021-9517/80/120383-08$02.00/0

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TABLE 1

Photoassisted Reactions on Semiconductor Oxides

$$1.\quad \left(\begin{array}{l} iC_4H_{10} + 2.5\,O_2 \xrightarrow[TiO_2]{h\nu} C_3H_6O + CO_2 + 2H_2O \\ \underset{TiO_2}{iC_4H_{10}} + 6.5\,O_2 \xrightarrow[TiO_2]{h\nu} 4CO_2 + 5H_2O \end{array}\right)$$

$$2.\quad CO + 0.5\,O_2 \xrightarrow[TiO_2,\ ZnO]{h\nu} CO_2$$

$$3.\quad CN^- + 0.5\,O_2 \xrightarrow[TiO_2,\ ZnO]{h\nu} CNO^-$$

$$4.\quad SO_3^{(2-)} + O_2 \xrightarrow[TiO_2,\ Fe_2O_3]{h\nu} \text{oxidized product}$$

$$5.\quad CH_3\,COOH \xrightarrow[TiO_2,1\text{-}5wt\%\ Pt]{h\nu} CH_4 + CO_2$$

$$6.\quad \text{Methylene blue (oxidized)} \xrightarrow[ZnO]{h\nu} \text{methylene blue (reduced)}$$

$$7.\quad \left(\begin{array}{l} N_2 + 3H_2O \xrightarrow[TiO_2]{h\nu} 2NH_3 + 1.5O_2 \\ N_2 + 2H_2O \xrightarrow[TiO_2]{h\nu} N_2H_4 + O_2 \end{array}\right)$$

$$8.\quad H_2O \xrightarrow[TiO_2]{h\nu} H_2 + \tfrac{1}{2}O_2$$

$$9.\quad \left\{\begin{array}{l} \text{Arochlor 254} \\ \text{2,4}'\text{-dichlorobiphenyl} \\ \text{2,2}'\text{-dichlorobiphenyl} \end{array}\right\} \xrightarrow[TiO_2]{h\nu} Cl^-,\ \text{dechlorinated products}$$

$$10.\quad CO_2 + 2H_2O \xrightarrow[SrTiO_3\ +\ Pt]{h\nu} CH_4 + 2O_2$$

of half-cell reactions represented by the example sequence

$$\begin{array}{l} A_{ads} + h^+ \rightarrow A^+{}_{ads} \\ B_{ads} + e^- \rightarrow B^-{}_{ads} \\ A^+{}_{ads} + B^-{}_{ads} \rightarrow \text{neutral products.} \end{array} \qquad (2)$$

If the kinetically slowest step in a dark reaction requires a hole, then the increase in hole concentration near the surface upon illumination will yield a corresponding increase in reaction rate. This is the photoassisted catalysis under discussion.

The selectivity with which the photogenerated hole is consumed is of primary importance. Three general possibilities exist:

(1) the photocatalysis of sequence 2;

(2) conversion of the original lattice,

$$\begin{array}{l} h^+ + \text{lattice site} \rightarrow (\text{lattice site})^+ \\ (\text{lattice site})^+ \rightarrow \text{lattice reaction product(s)} \end{array} \qquad (3)$$

(3) electron-hole recombination,

$$h^+ + e^- \rightarrow \text{thermal energy.} \qquad (4)$$

The relative rates of *catalysis, lattice conversion,* and *recombination* determine the efficiency of photon use for driving the desired catalytic reaction. Recombination always occurs; theoretical models of its contribution are treated elsewhere (*3, 23, 24*). When lattice conversion pre-

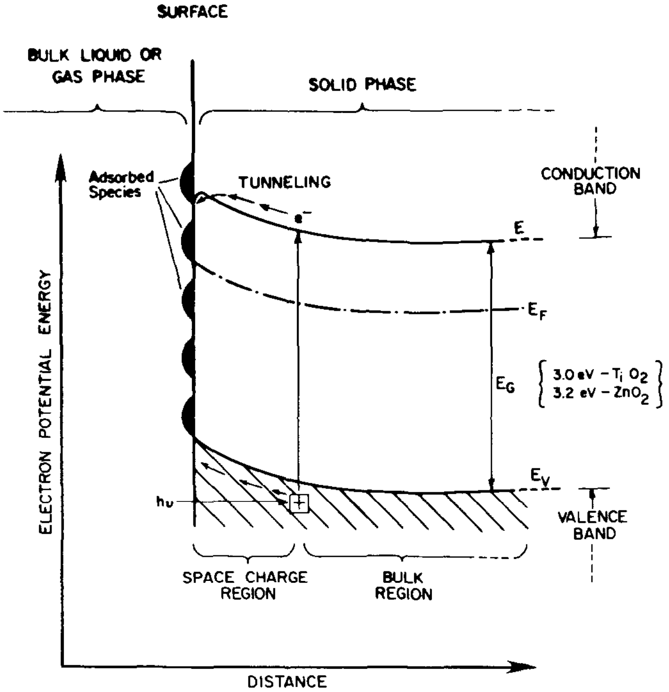

FIG. 1. Photoactivation of an *n*-type semiconductor catalyst (E_c = lowest conduction band level, E_v = highest valence band level, E_F = Fermi level, E_G = band gap of semiconductor ($= E_c - E_V$). Curved arrows indicate direction of net charge movement at steady state.

dominates, the solid is destroyed or continuously altered, i.e., the major product-generating reaction is *not* catalytic. With gas–solid systems, lattice conversion may result in changes in lattice nonstoichiometry or formation of new surface phases by reaction with adsorbates which were not present in the original lattice. In aqueous liquid–solid photoelectrocatalytic examples, not otherwise treated here (see Hager (*25*)), lattice conversion may include lattice dissolution. Our first question is thus whether sequence (2) or sequence (3) occurs on the solid.

BASIS FOR COMPARISON

Demonstration of catalysis and comparison of rates is best shown on a common basis. Similar concepts and quantities apply to both.

For an isothermal photocatalytic reaction, the rate depends on both the absorbed intensity of radiation (energy or photons absorbed per unit volume of catalyst per unit time) and the concentration of active sites on the catalyst surface. Taking the reaction to be first order in both intensity and active sites, a reasonable specific rate may be expressed as

$$r = \text{molecules reacted}/[(\text{time})(\text{active site})(\text{photon absorbed})].$$

This analog to the familiar turnover number (molecules/site · sec) of heterogeneous catalysis and the quantum efficiency (molecules reacted/photon absorbed) of photochemistry we shall call the "photocatalytic turnover number." When all terms in this expression are known, this quantity is an absolute scale for comparing activities of different catalysts.

Such a state of ideal knowledge does not usually exist. Here the surface concentration of active sites ordinarily is not known, a familiar situation in heterogeneous cata-

TABLE 2

Reaction (Ref)		Catalyst		Photon source		Experimental conditions								Results		Comparison	
[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]	[16]	[17]	[18]
	Solid	Modification^a	Surface area (m^2/g)	Lamp (W)	Intensity (photons entering reactors/sec)	Phase	Agitated?	1^b All catalyst irradiated?	Dark or homogeneous reaction?	Temperature (°C)	Initial concentration of reactant^c	Total reaction time (min)	Apparent quantum efficiency at (λ)	Fractional conversion	Highest rate (μmol/cm^2 · sec) × 10^5	Estimated turnover number^d (molecules/site · sec)	Turnovers accomplished^e (monolayers reacted)
1 (*4, 5*)	TiO$_2$ "P"	A	92	uv(NR)	1–7 × 10^{15}	G/S^f	N	Y	NN	25	37.5	150^g	1(3500)	0.037	1.73	2 × 10^{-2}	187
2 (*6*)	ZnO	NR	2.2	Hg(200)	1.4 × 10^{17}	G/S	N	N	Dark	200	40	NR	0.06(3650)	NR	0.43	5 × 10^{-3}	—
2 (*7*)	TiO$_2$^{h}	A/3%R	41	uv(NR)	NR	G/S	N	Y	NN	25	25	NR	NR	0.015	0.82	1 × 10^{-2}	—
3 (*8*)	TiO$_2$	A,u^i	≤1.54^j	Xe(450)	(5 × midday sun)	G/L/S – SL	Y	Y	NN	NR	1 × 10^{-3}	30	NR	0.54	≈0.39^k	5 × 10^{-3}	8
3 (*8*)	TiO$_2$	A,u^i	≤1.54^j	Hg–Xe(2500)	NR	G/L/S – SL	Y	Y	NN	NR	1 × 10^{-3}	1.67	NR	0.63	≈8.18^k	1 × 10^{-2}	10
3 (*8*)	TiO$_2$	A,u^i	≤1.54^j	Unfocused sunlight	NR^l	G/L/S	N	U	NN	NR	1 × 10^{-3}	2.9 × 10^3	NR	>0.99	≈0.008^k	1 × 10^{-4}	17
3 (*9*)	TiO$_2$^{m}	A,u	≤1.54^j	Xe(450)	NR	G/L/S – SL	Y	Y	NN	NR	1 × 10^{-3}	60	NR	0.77	≈0.20^n	2 × 10^{-3}	9
3 (*9*)	TiO$_2$^{m}	A,u	≤1.54^j	Unfocused sunlight	NR	G/L/S	N	N	NN	NR	3 × 10^{-2}	3.3 × 10^4	NR	0.80	≈0.31	4 × 10^{-3}	7330
3 (*9*)	ZnO	NR	1.07^j	XE(450)	NR	G/L/S – SL	Y	Y	NN	NR	1 × 10^{-3}	60	NR	0.95	≈0.24	3 × 10^{-3}	10
4 (*9*)	Fe$_2$O$_3$	α phase	1.15^j	Xe(450)	NR	G/L/S – SL	Y	Y	NN	NR	1 × 10^{-3}	6	NR	≈0.95	≈6.09^o	7 × 10^{-2}	26
4 (*9*)	TiO$_2$	A,u	≤1.54^j	Xe(450)	NR	G/L/S – SL	Y	Y	NN	NR	1 × 10^{-3}	10	NR	≈0.74	≈0.65	8 × 10^{-3}	5
5 (*10*)	TiO$_2$	A,Pt	1–10^p	Xe–Hg(1600)	NR	L/S – SL	Y	Y	NEG	55	1.59	NR	NR	—	≈2.^{q}	2 × 10^{-2}	—
5 (*11*)	TiO$_2$	A,u	1–10^p	Xe–Hg(2500)	NR	L/S – SL + O$_2$	Y	Y	NR	55	5	300	NR	0.8 × 10^{-3}	≈1.	1 × 10^{-2}	216
5 (*11*)	TiO$_2$	A,u	1–10^p	Xe–Hg(2500)	NR	L/S – SL + O$_2$	Y	Y	NR	42	5	180	NR	0.3 × 10^{-3}	≈0.8	1 × 10^{-3}	104
5 (*11*)	TiO$_2$	A,Pt	1–10^p	Xe–Hg(2500)	NR	L/S – SL + O$_2$	Y	Y	NR	55	8 × 10^{-1}	120	0.095(NR)	5 × 10^{-3}	≈3.	4 × 10^{-2}	259
5 (*11*)	TiO$_2$	A,d,Pt	1–10^p	Xe–Hg(1600)	NR	L/S – SL	Y	Y	NR	55	Glacial H Ac	66	NR	1 × 10^{-3}	≈5.	6 × 10^{-2}	238
5 (*11*)	TiO$_2$	A,d,Pt	1–10^p	Xe–Hg(1600)	NR	L/S – SL	Y	Y	NR	45	H Ac + NaAc	162	NR	2 × 10^{-3}	≈3.	4 × 10^{-2}	350
5 (*11*)	TiO$_2$	A,d,Pt	1–10^p	Xe(450)	NR	L/S – SL	Y	Y	NR	55	H Ac + NaAc	222	0.07(NR)	0.3 × 10^{-3}	≈0.4	5 × 10^{-2}	47
5 (*11*)	TiO$_2$	A,d,Pt	1–10^p	Unfocused sunlight	NR	L/S – SL	NR	Y	NR	25	Glacial H Ac	73 × 10^4	NR	4 × 10^{-3}	≈0.06	7 × 10^{-4}	9
6 (*12*)	ZnO	NR	0.02–0.1^j	Hg(low pressure)	4 × 10^{13}/cm^3	L/S – SL (0.5 wt%)	Y	U	NR	31.9	4.55 × 10^{-5}	40	0.1(3650)	0.42	≈0.3^r	4 × 10^{-3}	3740
6 (*12*)	ZnO	NR	0.02–0.1^j	Hg(low pressure)	4 × 10^{13}/cm^3	L/S – SL (1.5 wt%)	Y	U	NR	31.9	4.55 × 10^{-5}	40	0.073(3650)	0.50	≈0.1^r	1 × 10^{-3}	3
6 (*12*)	ZnO	NR	0.02–0.1^j	Hg(low pressure)	4 × 10^{13}/cm^3	L/S – SL (6.0 wt%)	Y	U	NR	31.9	4.55 × 10^{-5}	40	0.062(3650)	0.65	≈0.03^r	4 × 10^{-4}	1

7 (*13*)	TiO_2	0.2 wt% Fe_2O_3[s]	1.4–2.8[j]	Hg(360)	NR	G/S(N_2)	N	N	NN	50	440[t]	120	NR	≈0.11[u]	≈0.2[q]	2×10^{-3}	14
8 (*13*)	TiO_2	0.2 wt% Fe_2O_3[s]	1.4–2.8[j]	Hg(360)	NR	G/S(Ar)	N	N	NN	50	440[t]	60	NR	≈0.08[u]	≈0.3[q]	3×10^{-3}	8
9 (*14*)	TiO_2	NR	NR[q]	Blak Ray	NR	L/S – SL	NR	U	NN	NR	1.12×10^{-4}	30	NR	1.00	≈0.0001[q]	1×10^{-6}	2×10^{-3}
10 (*15*)	$SrTiO_3$+Pt	Single crystal	1 cm^2	Hg(500)	$\approx 10^{17}/cm^2$	G/S	Y	Y	Y	<42	CO_2 = 47[v] H_2O = 53	10	10^{-4}(near uv)	3×10^{-4}	5.53[w]	6.7×10^{-2}	5 – 10[x]

[a] A, Anatase; R, rutile; u, undoped, d, doped; Pt, platinized.

[b] Based on 2 μm light penetration for catalyst layers.

[c] Gaseous reactant, mole %; liquid reactant, moles/liter.

[d] Based on 5 × 10^{14} sites/cm^2 catalyst.

[e] Turnovers accomplished = (turnover number) × (reaction time).

[f] G, gas; S, solid; L, liquid; Sl, slurry; N, no; Y, yes; NR, not reported; NN, none; NEG, negligible; U, unknown; ----, insufficient information to calculate.

[g] Longest reported.

[h] Also Ga_2O_3, SnO_2, ZnO_2.

[i] Also A,d; R,d; R,u.

[j] Estimated from reported particle size, assuming spherical particles.

[k] Based on lowest reported catalyst loading (0.05 g/10 ml solution).

[l] Reference given.

[m] Also ZnO and CdS.

[n] Initial rate—decreased after 30 min.

[o] Initial rate—decreased after 1 min.

[p] Assumed from Ref. (*12*).

[q] All rates for reactions 5, 7, 8, and 9 based on 2 m^2/g.

[r] Based on 0.6 m^2/g.

[s] Doped with Fe_2O_3; 23% R, 77% A.

[t] H_2O content of sample (μmol/gcat).

[u] Based on H_2O content of entire mass of catalyst.

[v] Total pressure = 32 Torr.

[w] Initial rate (rate halted after 10 min).

[x] *Reported* values based on total methane production and surface site density of $SrTiO_3$.

lytic kinetics. The absorbed intensity for photocatalytic reactions refers strictly to absorption by the solid ($I_{abs,cat}$); photons absorbed by the fluid are presumed not to contribute. The quantity $I_{abs,cat}$ depends on reactor geometry, wavelength, inhomogeneity of reaction mixture and absorption coefficients. It is difficult to predict. Photon absorption rates of semiconductor electrodes can be inferred from electrochemical measurements of photocurrent density, but are a strong function of the doping or impurity levels of the solid. It is unlikely that different uncharacterized samples will have the identical photoabsorptive properties. In the absence of fundamental information, the photocatalytic turnover number should be referred to quantities which can be experimentally determined: the total surface area of the catalyst and the rate of photons entering the reaction volume.

For photocatalytic reactions, the surface area of the irradiated volume of catalyst is the proper basis, since any solid not irradiated will be inactive. The intensity profile of a photon source in an absorbing medium is related to the incident intensity by the Beer–Lambert equation

$$\log(I_0/I) = \text{Absorbance} = \mu x.$$

The absorption coefficient, μ, of powdered solids is not easily determined. For a layer of powder, Fig. 2 implies that a typical penetration depth of uv light into TiO_2 powder is about 2 μm (*4*). Alternately, μ^{-1} provides an estimate of penetration. The surface area of material in this illuminated volume is the quantity sought for the turnover number estimate.

The rate of photons entering the reactor can be determined by standard actinometric or photometric methods, although absorption, scattering, and reflection effects of the solid are not usually accounted for. While this approach lacks the appeal of fundamental understanding of the solid/photon interaction, it does provide the number of reaction events per entering

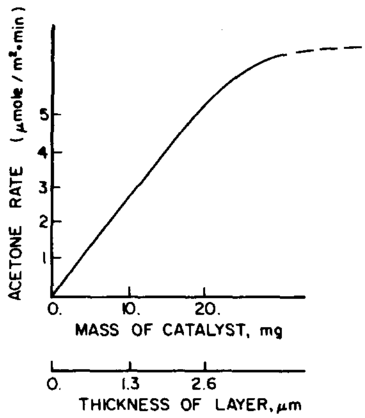

FIG. 2. Acetone production rate versus depth of powdered catalyst layer. Teichner *et al.* (*4*) report a critical mass of 17 mg for TiO_2 (anatase) corresponding to a penetration depth of approximately 2 μm.

photon, i.e., apparent quantum efficiency of the system.

CATALYSIS?

We have looked for the answers to our questions in some published data for reactions termed photocatalytic. The original data, along with our estimates or calculations, are summarized in Table 2. We note specific information about the catalysts and sources of illumination. Where surface areas were not reported, we estimated them from the particle size. The rates are expressed both as activities (μmoles/$cm^2 \cdot$ sec) and turnover numbers; the conversions as fractional conversions and turnovers accomplished.

With few exceptions, noted in Column 6, the photon input rate was not reported. Thus, photocatalytic turnover numbers could not be extracted from these data.

On the common basis of irradiated surface area, we can estimate not only whether these reactions are catalytic, but also how their rates compare with commercial and biological catalysts. The turnovers accomplished (Column 19) represent the number of molecules reacted per surface site, based on a catalytic site concentration of $5 \times 10^{14}/cm^2$. This quantity may be regarded as indicative of whether the reaction is catalytic or stoichiometric with the surface. *As a guideline, a turnover of less than unity definitely has not proven the existence of catalysis, and somewhat arbitrarily, turnovers larger than 100 probably have. From Column 18, claims of catalysis are thus open to question for many of these studies.* Almost half of the turnovers accomplished lie in the dubious region between 1 and 100. Vague statements that "the catalyst was active for several hours" or "was recovered after reaction" do not prove the case.

Despite the uncertainty brought by the assumptions underlying Table 2, it is intriguing to compare these turnover numbers to typical industrial values. Some reactions with turnover numbers which are well established are shown in Table 3. The range

TABLE 3

Turnover Numbers for Some Commercial and Biological Catalysts

Reaction (Ref)	Catalyst	Temperature	Turnover/sec
H_2 oxidation (*15*)	Metal oxides	300°C	10^{-7}–10^{-2}
Naptha reforming (*16*)	0.35% Pt/Al_2O_3[a]	940°F	≈1
Fluid catalytic cracking (*16*)	15% REY/Al_2O_3[b]	975°F	≈30
Oligomerization of *i*-butylene (*17*)	Amberlyst 15 ion exchange resin	60°C	≈3
Biological reactions (*18*)	Enzymes	0–31°C	10^{-3}–10^{5}
Photocatalytic reactions (Table 2)	TiO_2,ZnO	25–55°C	≈10^{-4}–10^{-1}

[a] Typical operating conditions: 2WHSV, 100% conversion, fraction Pt available ≈0.2.

[b] Typical operating conditions: 8 : 1 Cat : OIL, 10% conversion, 15 sec residence time.

TABLE 4

Information Needed to Compare Photocatalysis

Required:	Mass balance Surface area/mass catalyst Photon absorbtion rate (or equivalent, e.g., reactor flux)
Also useful:	
Classical kinetics:	Balanced reactions, product identifications, feed composition, reaction time, conversion, temperature, checks for dark or homogeneous reactions
Catalyst characterization:	Crystal phase, doping level, pretreatment
Radiation:	Lamp power, spectral distribution, reactor geometry and dimensions

spans several orders of magnitude, and the rates of Table 2 lie in the lower end, at 10^{-4}–10^{-1} turnovers/sec. The statement is sometimes made that a good industrial catalyst has a turnover number of order one.

What happens when we examine our active site approximation of $5 \times 10^{14}/\text{cm}^2$? If, as Morrison suggests (*20*), hydroxyl groups on the partially reduced titania surface were active sites, then that number is reasonable. If the active sites for semiconductor photocatalysis were defect or dopant sites, or were sites arising from depletive chemisorption (*21, 22*), then their concentration could be about $10^{12}/\text{cm}^2$. In that case, the turnover numbers of Table 2 would increase to 10^{-1}–10^2, and the case for catalysis would be correspondingly strengthened. The value of 10^{-1} would then be characteristic of the solar-irradiated experiments for *n*-type semiconductors for the lower active site concentration.

Development of quantitation in heterogeneous catalysis required appropriate surface characterization before rates could be reported on a common basis. For photoassisted catalysis, there is an additional requirement to determine quantum efficiencies. In Table 4, we list the basic information necessary to evaluate photocatalytic reactions. The two quantities essential for computing photocatalytic reaction rates, namely, surface areas and photon absorption rates, are those most typically omitted to date. The field of photoassisted catalysis will obviously mature as comparisons can be made on a standard basis.

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