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Is There a Particle-Size Dependence for the Mediation by Colloidal Redox Catalysts of the Light-Induced Hydrogen Evolution from Water?[‡]

P. Keller and A. Moradpour*

Contribution from the Laboratoire de Physique des Solides and Laboratoire de Synthèse Asymétrique, Université de Paris-Sud, 91405-Orsay, France. *Received June 4, 1980*

Abstract: Particle-size effects for the catalysis by platinum of the light-induced hydrogen evolution from water, using the $(Ru(bpy)_3{}^{2+}$/methyl viologen/EDTA) model system, were investigated with widely polydispersed colloidal platinum hydrosols and samples with narrower size distributions obtained from the former hydrosols by centrifugation. The optimum values for the hydrogen-formation rates and yields were found to be very similar for all catalysts studied; this was true for those containing polydispersed or selected small (<100 Å) as well as large particles (>1000 Å). In fact, no platinum particle-size effects on the methyl viologen mediated hydrogen evolutions were observed in the investigated size range. These results are discussed in relation to studies on catalyst-dispersion effects in the field of heterogeneous catalysis.

Introduction

Heterogeneous catalysts, i.e., Pt and RuO_2, are currently being studied intensively as components of hydrogen[1] and oxygen[2] generating systems in the development of water-splitting light-energy storing processes. Platinum-metal colloidal hydrosols, known for a long time as hydrogenation catalysts,[3] were recently introduced by us[1c] as the fourth component of a $(Ru(bpy)_3{}^{2+}/MV^{2+}/EDTA)$ (MV^{2+} = methyl viologen) hydrogen-generating model system. Simultaneously, others[1d] proposed PtO_2 as part of a similar photosystem. However, other investigators have demonstrate potential problems with PtO_2,[4] and more recent studies[5] have focused on the use of platinum as a colloidal solution.

Any simple single-phase combinations of the components of these half-cell models[1,2] in tentative efforts[2b] to split water into hydrogen and oxygen obviously require exceedingly efficient redox catalysts. A recent report in this journal[6] emphasized the use of particle-size effects as a possible way to obtain these high efficiencies: colloidal platinum having particle radii of 110 Å was claimed to be exceptionally active in promoting hydrogen evolution from water. This apparently straightforward result is evidently based on a limited number of data; we wish to report here a systematic study of particle-size effects on methyl viologen-mediated photochemical hydrogen generation which indicates no *net* size effect over a wide range.

Experimental Section

The chemicals were of commercial grade purity and were used without further purification; methyl viologen (Sigma) was dried and stored under vacuum over P_2O_5. The colloidal platinum hydrosols (Sol.R) were prepared according to published procedure;[3] the stabilizing polymer was poly(vinyl alcohol) (PVA) (Baker, viscosity of a 4% aqueous Solution: 55–65 cP and the reducing agent was hydrogen (24 h at room temperature and atmospheric pressure). Fractionations of these colloidal catalysts as a function of the particle size were effected by centrifugation.[7] (i) Ten-milliliter aliquots of Sol.R were centrifuged (Beckman J 21 B centrifuge) for 24 h at 20 000 rpm (48 300 g); the upper 5 mL were carefully syringed out and gave the light brown Sol.A. (ii) Operating at 12 000 rpm (25 000 g) for 8 h, we isolated heavy, precipitated particles embedded in sedimented PVA polymer and resuspended them in water, giving Sol.B. The described results were obtained with centrifuged catalysts prepared from the same starting colloidal solution. Otherwise, if different batches are centrifuged, significant differences may occur in the amounts of sedimented heavy particles, depending on the ageing of the solutions. A comparable clustering phenomenon has already been observed with Pd solutions.[7]

The particles sizes were measured on electron micrographs (Phillips EM 300 instrument) with platinum particles deposited on carbon films. A clear size segregation was observed after centrifugations: uncentrifuged, widely polydispersed Sol.R led to Sol.A which contained small particles (all observed particles were smaller than 40 Å and an average size of 16 Å was calculated by measuring the size distribution of a collection of 550 particles) and to Sol.B which contained sedimented large aggregates (average size above 1000 Å). The platinum contents of the various catalyst solutions were determined (within 5%) by atomic absorption spectroscopy at the CNRS. Service Central de Microanalyse: Sol.R = 1.79×10^{-3} M; Sol.A = 0.43×10^{-3} M; Sol.B: 0.16×10^{-3} M (aliquots of catalysts solutions were evaporated, platinum aggregates redissolved in aqua regia, and samples diluted with water to the required volume prior to the measurements). Irradiations were carried out with 30 mL of aqueous solutions deaerated by argon bubbling (acetate buffer, 0.5 M, pH 5) containing the required amounts of the components with a Rollei P 360 slide projector equipped with a 250-W halogen lamp.[8] The evolved gases were bubbled through a 50% potassium hydroxide solution, before the volume measurements were recorded (within 10%), by using the previously described[8,9] gas volumeter; the rates and the yields of hydrogen formation were thus calculated from the slopes and plateau values of the resulting graphs. Hydrogen was analyzed by GLC (molecular sieves at room temperature).[1c,8b]

The hydrogenations (1 atm H_2) of methyl viologen were studied in aqueous solutions (acetate, pH 5, and phosphate, pH 7, buffers) with Sol.R, Sol.A, and PtO_2 as catalysts. With use of the latter, the far most active in this case,[10] a very efficient hydrogenation reaction took place (6 mol of H_2/mol of methyl viologen were absorbed); the resulting high yield compound was readily isolated and identified as *N,N′*-dimethyl-4,4′-bipiperidine.[11]

The amounts of methyl viologen present in the hydrogenation studies were determined by high-pressure LC. These analyses were performed

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(10) The extremely low hydrogen-evolution rates and yields obtained photochemically by using the same PtO_2[4] catalyst, compared to colloidal platinum hydrosols,[8b] are certainly related to this high methyl viologen-hydrogenation efficiency.

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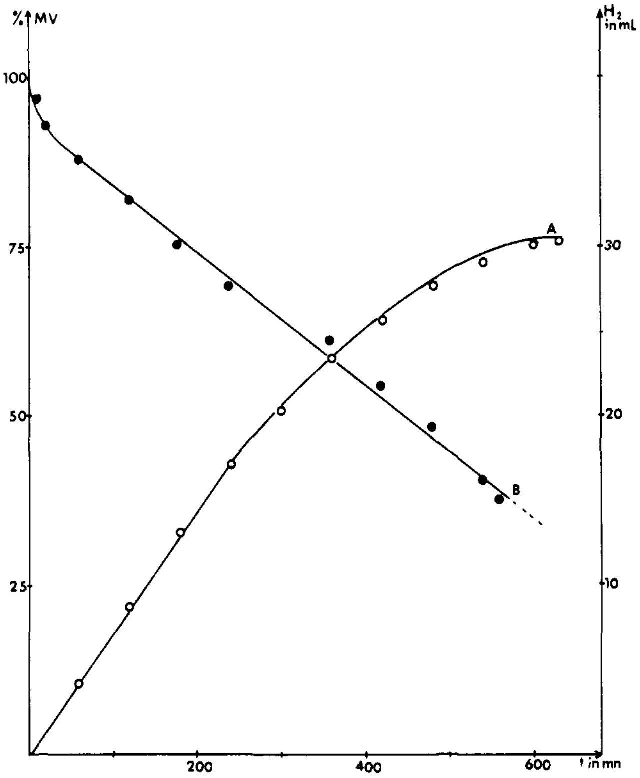

Figure 1. Hydrogen-formation rate and yield as a function of irradiation time and the corresponding analysis of MV^{2+} using high-pressure LC irradiated solution (30 mL, acetate buffer, 0.5 M, pH 5) contained 1.5×10^{-5} mol of MV^{2+}; 6×10^{-3} mol of EDTA; 6×10^{-6} mol of $Ru(bpy)_3^{2+}$, and 7×10^{-7} mol of platinum (Sol.R)): curve A, volumes of hydrogen formed as a function of time; curve B, amounts of MV^{2+} remaining in the irradiated mixture, as a function of time, determined by high-pressure LC analysis.

on an analytical instrument (Waters Ass.) equipped with a spectrophotometric detector (detection wavelength = 254 nm) with a μ Bondapak C 18 column (Waters Ass.); a pH 5 phosphate buffer (80%)/methanol (20%)/PIC B7 reagent (Waters Ass.) mixture was used as eluant[12] (flow rate = 1 mL × $\min^{-1}$; retention volume of methyl viologen = 4.4 mL).

Results and Discussion

The mechanism of the photochemical generation[1c,d,13,14] of reduced methyl viologen $MV^{+}\cdot$ obtained by visible-light irradiations of aqueous deaerated solutions containing $Ru(bpy)_3^{2+}$ as a light absorbing species and EDTA as an electron source, as well as the possibility of simultaneous hydrogen evolution through a platinum-catalyzed process (equilibrium 1), has been well established.[1c,5,8] In our previous reports[8] we have found a factor which limited the overall yields of the hydrogen produced by this photosystem. In a typical experiment reported in Figure 1 hydrogen was first generated at a constant rate and then gas productions slowly decreased and finally spontaneously stopped (curve A). As the reaction proceeded, the amounts of methyl viologen were measured by high-pressure LC analysis (curve B). In fact, these amounts decreased sharply, the gas evolutions stopping when nearly all MV^{2+} had disappeared. Thus an irreversible side-reaction took place which destroyed the electron relay. This was found to be a platinum-dependent hydrogenation (reaction 2)

$$MV^{+}\cdot + H^{+} \underset{Pt}{\rightleftharpoons} MV^{2+} + {}^{1}/{}_{2}H_2 \qquad (1)$$

$$MV^{2+} \text{ (or } MV^{+}\cdot) \xrightarrow[Pt]{H_2} \text{reduction product} \qquad (2)$$

which led to the completely reduced bipiperidine derivative.

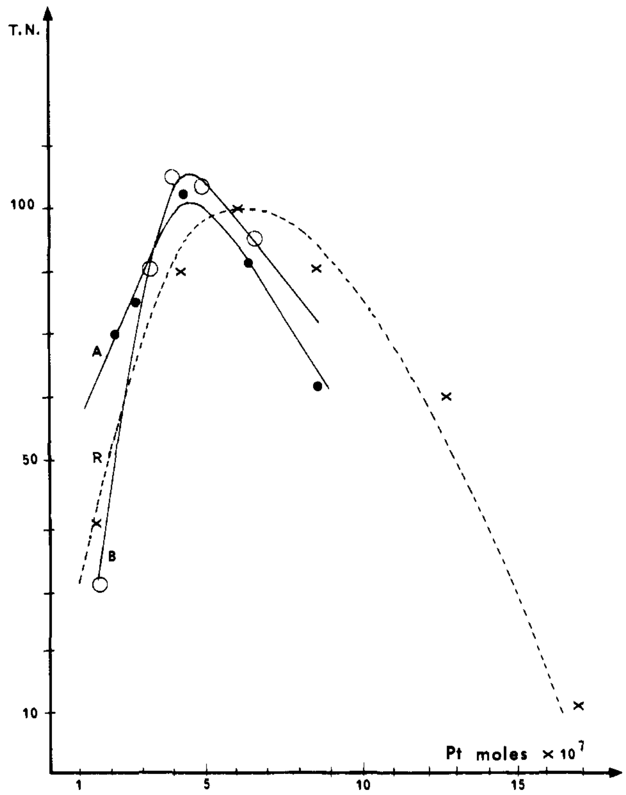

Figure 2. Methyl viologen turnover numbers (TN) as a function of the added amounts of the colloidal platinum particles of different size distributions; irradiation conditions specified in Table I, note a; turnover numbers defined as the ratios of the total amounts of obtained hydrogen (Table I) and the initial amount of methyl viologen: [×] curve R, catalyst used = Sol.R (uncentrifuged); [●] curve A, catalyst used = Sol.A (centrifuged, average size = 16 Å); [○] curve B, catalyst used = Sol.B (centrifuged, mean particles size > 1000 Å).

Clearly, the overall catalytic efficiency toward hydrogen generation of the colloidal platinum, which is operating in a crucial rate-determining step (vide infra), is ultimately determined by the relative efficiencies (rates) of two competing successive hydrogen-forming (equilibrium 1) and hydrogen-consuming (reaction 2) catalyzed reactions. Taking into account the existence of these competing processes, we have investigated the possibility of a catalyst-dispersion effect on the efficiencies of the photochemical hydrogen productions.

The hydrogen-evolution rates and yields, using all three catalyst solutions (Sol.R, Sol.A, Sol.B), were measured as a function of the added amount of platinum (Table I). Both factors were sharply dependent on this parameter, as already observed[8] by using Sol.R (Table I, entries 1–6 R): (i) the rates were primarily determined by the added catalyst amounts and therefore pointed out the fact that a platinum-centered step (and not, i.e., the photon flux) is rate determining in the overall hydrogen-formation process, under our conditions; (ii) the yields of the hydrogen productions varied also in this way and were improved by about 1 order of magnitude by simply adjusting the catalyst amount. Remarkably, now using larger particles (Sol.B, entries 12–16 B) as well as small ones (Sol.A, entries 7–11 A), we noticed the same behavior. In all cases, the measured hydrogen-formation rates and yields increased to a maximum value, when the amount of colloidal platinum was increased, and then decreased as solutions containing higher concentrations of platinum were irradiated. The optimum values for the rates and the yields and consequently the optimum turnover numbers for the MV^{2+} electron relay (Figure 2) were found to be very similar for all studied catalysts and were obtained with a comparable amount of platinum (entries 3 R, 9 A, and 14 B). Clearly, the measured *maximum catalyst efficiencies* remained almost constant disregarding the size distributions.[15]

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Table I. Rates and Yields of the Hydrogen Evolutions[a] as a Function of the Colloidal Platinum Size Distributions

entry[b]	Pt amounts, mol × 10^7	H_2[c] formation rates, mL h^{-1}	H_2[c,d] formation yields, mmol
1 R	1.70	3.6	0.60
2 R	4.25	4.4	1.20
3 R	5.95	4.5	1.35
4 R	8.50	4.6	1.20
5 R	12.70	2.8	0.90
6 R	17.90	1.8	0.20
7 A	2.15	4.2	1.10
8 A	3.0	4.6	1.15
9 A	4.30	4.0	1.40
10 A	6.45	4.1	1.20
11 A	8.60	2.7	0.90
12 B	1.60	2.3	0.45
13 B	3.20	4.5	1.20
14 B	4.0	4.1	1.42
15 B	4.86	3.5	1.40
16 B	6.48	3.1	1.28

[a] 30 mL of solutions (acetate buffer pH 5) containing $Ru(bpy)_3^{2+} = 6 \times 10^{-6}$ mol, $MV^{2+} = 1.5 \times 10^{-5}$ mol, and EDTA = 6×10^{-3} mol were irradiated. [b] The letters R, A, and B correspond to the various colloidal solutions used: Sol.R, Sol.A, and Sol.B (see Experimental Section). [c] The hydrogen-formation rates and yields were measured as previously described,[1c,8b] within 10%. [d] The indicated yields correspond to the total amounts of hydrogen obtained after the reaction had spontaneously stopped.

However, the predictable proportionality of the catalyst activity to the particle surface areas was in fact observed, for example, in hydrogenation experiments using centrifuged colloidal palladium particles.[7] Therefore, the possible interference of particle size factors was also examined on the more simple two-component system (MV^{2+}/Pt) under hydrogen. This system also includes unavoidably interrelated hydrogen-involving steps (equilibrium 1 and reaction 2), the reactive intermediate $MV^{+}\cdot$ being now produced catalytically by a pH-dependent reaction (equilibrium 1). This time, the MV^{2+} hydrogenations (reaction 2) were studied by using Sol.R and Sol.A as catalysts. A slightly higher hydrogenation rate was observed (Figure 3) by using the small aggregates (curve A) as compared to the uncentrifuged colloidal catalysts (curve B). As a matter of fact, this small effect, not detected with the above photochemical hydrogen generations, may possibly indicate that the unknown total surface areas of the present particle-size distributions (Sol.A vs. Sol.R) are simply not significantly different.

In any case, the present results show that there is no special advantage, with this photochemical system, to isolate out of the available colloidal solutions platinum particles of a particular size and to focus on any size factors in the investigated range. In fact, closely comparable hydrogen-evolution rates and yields may be obtained after the required amount of platinum had been added, the bubbling of gas occurring under illumination being readily observable in every case.

Would it be possible to observe a *specific* particle-size effect on these reactions? In this respect, the considerable amount of work in the field of heterogeneous catalysis must not be overlooked. As a matter of fact, the catalyst-dispersion effects on reaction rates, as a major problem in this field, have been searched for a long time,[16] and systems were classified, according to Boudart's terminology,[17] as "structure sensitive" (when exhibiting dependence on size effects) and "structure insensitive". However, for most catalytic reactions investigated, the specific reaction rates and selectivities (when several different possible reaction mechanisms existed) remained remarkably constant, that is, independent of catalyst dispersion. To our knowledge, very few examples of "structure-sensitive" reactions had been discovered, and these were mainly skeletal isomerizations.[16c] It is noteworthy that the reaction-rate variations, as a function of catalyst size, were clearly assigned[16,18] to metal aggregates 1 order of magnitude smaller than the considered ones.[6]

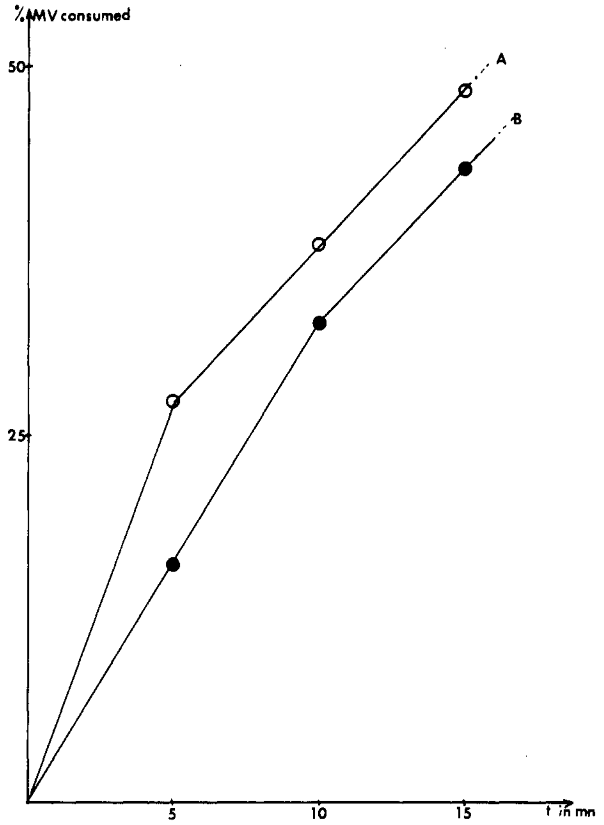

Figure 3. The hydrogenation of methyl viologen catalyzed by colloidal platinum as a function of the particle size (30-mL solutions (phosphate buffer, 0.5 M, pH 7) containing 0.75×10^{-5} mol of MV^{2+} and 1×10^{-6} mol of platinum kept under hydrogen; the concentrations of remaining MV^{2+} determined by high-pressure LC analysis; the ratio of hydrogenated MV^{2+} calculated and plotted as a function of time); curve A, catalyst used = Sol. A; curve B, catalyst used = Sol.R.

Thus, the demonstration of particle-size effects on the photochemical hydrogen evolutions and the resulting efficiency improvement of the investigated redox catalysts, involving methyl viologen as an electron mediator, need further study. The use of pure-metal colloidal solutions may not be the best way to achieve the required high-dispersion catalysts: the study of supported catalysts may be one worthwhile possibility in this direction. However a better electron mediator and a more simple reaction scheme would certainly be more suitable for these studies and for the detection of such effects. As a matter of fact, differences in catalysts surface areas (i.e., a factor of 60 is calculated as the ratio

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(15) This conclusion is in complete disagreement with the already cited[6] report on the catalysts size factors; the authors examined the influence of different catalyst preparations on a limited aspect of the hydrogen evolutions, namely, formation *rates*. In fact, hydrogen production *yields* and more importantly the platinum-concentration dependence of both parameters were ignored and the work was done in an almost "unfavorable" platinum concentration range, as compared to our results. An accurate comparison of the values of rates reported in the referred work[6] with ours is difficult mainly because of different experimental conditions (light sources, sample sizes, concentrations, etc). However, the orders of magnitude may be compared: converting the values (expressed in mL h^{-1} per 30 mL of solutions; Table I) to the same units (L day^{-1} per L of solution[6]) our rates fall in the (1–4) L × day^{-1} per L range ((2–12) L day^{-1} per L in ref 6).

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between the total available surface area of particles of respectively 16 and 1000 Å in diameter, assuming spherical shapes for all particles as a rough approximation) and in catalysts surface "concentrations" (going from small to large particle) may introduce some kinetics effects, especially in cases where there are short-lived intermediates.

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A QSAR Investigation of Dihydrofolate Reductase Inhibition by Baker Triazines Based upon Molecular Shape Analysis

A. J. Hopfinger

Contribution from the Department of Macromolecular Science, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio 44106. *Received March 3, 1980*

Abstract: Three-dimensional molecular shape descriptors have been defined for a set of Baker triazines which are dihydrofolate reductase (DHFR) inhibitors. Two shape descriptors, and one physicochemical feature, the sum of the 3- and 4-substituent octanol/water fragment constants, are needed to explain a range in activity in the data base of 5.11 log $(1/C)$ units. C is the molar concentration of triazine for 50% in vitro inhibition. One of the molecular shape descriptors, S_0, is proportional to the common overlap steric volume between pairs of molecules. The other shape descriptor, D_4, is a measure of the length of the 4-substituent in a triazine molecule. The compound data base consists of 27 compounds selected to represent each possible conformational class of compounds within the set of Baker triazines. No compound in the data base had to be eliminated as an outlyer. The quantitative structure–activity relationships (QSARs) generated in this study are tested on seven known compounds and used to predict five active compounds. This study constitutes, perhaps, the clearest instance to date where the consideration of molecular shape/conformation leads to an improved quantitative description of drug potencies.

Introduction

Two major obstacles have impeded quantitatively employing conformational analysis in drug design. First there is the problem of being able to identify the stable conformers of flexible molecules. A significant breakthrough in this area has been the development of molecular mechanics.[1,2] The decisive practical advantage of doing conformational analysis using molecular mechanics methods, as opposed to molecular orbital theory,[3] was first shown by our laboratory for some phenethylamines.[4] The general utilization of molecular mechanics calculations for molecular structure determination has been realized in our software package, currently called CAMSEQ-II.[5] Technical progress to explore larger and more flexible molecules has come from a new generation of low-cost, high-speed "super-mini" computers.

The other obstacle to conformation-dependent, quantitative drug design is the characterization of molecular shape. At this point let a formal distinction be made between shape and conformation. Conformation is a component of shape in that conformation defines the location of atoms in space. The properties of these atoms, most notably their "sizes", represent an additional set of factors needed to specify molecular shape. A theory of molecular shape analysis is outlined in this paper.

Some structure–activity studies have employed conformational features. These include: (1) an interatomic distance within a molecule,[3,6,7] (2) a set of interatomic distances within a molecule,[3,8–10] (3) a set of atomic coordinates within a molecule,[4,11] and (4) a set of critical intermolecular binding distances.[12] Simple shape descriptors, which include (1) molecular volume,[13] (2) molecular surface area,[14] and (3) spatial potential surfaces of a molecule with respect to a test species[15,16] have also been considered in establishing structure–activity relationships.

Each of these descriptors, except the last, only provides a *partial* representation of the overall shape of a molecule. Spatial potential surfaces do reflect overall molecular shape, but a means representing this information for quantitative comparison is not reported.

A general theory of comparing molecular shapes is being developed in our laboratory. Molecular shape descriptors derived from this theory have been applied to quantitatively explain the observed 50% in vitro inhibition activity of a dihydrofolate reductase enzyme assay by a set of Baker triazines.[17] The purpose of this paper is to report this study which represents a clear instance where a systematic consideration of molecular shape leads to a quantitative structure–activity relationship (QSAR) superior to a QSAR derived only using physicochemical and substructural features.[18]

Silipo and Hansch pioneered in the structure–activity analysis of the Baker triazines.[18] Hansch and co-workers have continued in the structure–activity development of triazine inhibitors of dihydrofolate reductases (DHFR)s.[19,20] Silipo and Hansch suggest that the Baker triazine data base serve as a "standard" for evaluating quantitative structure–activity methods.[18] We adopted this suggestion and carried out our first study of some Baker

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