CORRESPONDENCE

Concerning Catalysis of Photochemical Reactions

In a recent Account by Wubbels[1] a definition of a catalyst of a photochemical reaction is proposed and a number of reactions are accordingly examined. In the interest of still greater consistency, some considerations are appropriate.

(1) The catalytic effect should be expressed,[2] as in thermal chemistry, in terms of rate constant ($k_r^c[C]$ vs. k_r) rather than, as proposed (p 286), in terms of quantum yield. In this way an enhancement of the reaction quantum yield

$$\Phi = \eta \left(\frac{k_r^c[C] + k_r}{k_d + k_r^c[C] + k_r} \right)$$

due to an increase of the reaction rate can be distinguished from an enhancement due to an effect of the catalyst C on η or k_d without requiring additional stipulation (p 287), and the reactivity of different excited states can be compared in terms of reaction rate, while this would be misleading in terms of quantum yield. Efficiency for a photoreaction is the quantity usually determined, but is not "the analogue of rate for a ground-state reaction".

(2) Contrary to what Wubbels stated, there is a reason "why a reaction originating in an excited state cannot be catalyzed", and that is the short lifetime of excited states. This limits the type of possible catalyst–substrate interaction to very fast phenomena, in practice electron and proton transfer, while absorption equilibria and metal complexation are excluded (unless of course a preexisting complex is irradiated).

(3) Even with this limitation, only a part of the examples discussed implies a direct interaction of the catalyst with the excited state (electron transfer, ref 41, 42, 50, 52, or proton transfer, ref 38 and possibly 45) or with an exciplex (ref 28, 29, 54). In the other cases the catalyst acts on the primary photoproduct, be it a reactive particle, such a a σ complex or a radical (ref 20, 27, 32a, 37) or a strained, but certainly ground-state molecule (ref 32b, 33, 34, 35, 36, 43, 46). Rather than catalysis of a photochemical reaction, one has here catalysis of the reaction of products previously formed by photochemical means. More examples could be quoted for each category, but the fact remains that the largest number will be found in the last one.

(4) In the meanwhile, other groups have proposed definitions correlating homogeneous catalysis and photochemical reactions,[3] while the situation is more confused for heterogeneous phenomena. As all these fields are rapidly growing, a common effort to offer an univocal terminology would be appropriate.

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(1) Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285–292.
(2) In the following, k_r is the rate of the photochemical process, $k_r^c[C]$ the rate of the corresponding catalyzed process, η the efficiency of formation of the reactive excited state from the state initially formed by absorption, and k_d the cumulative rate of unproductive decay from such state.
(3) Salomon, R. G. *Tetrahedron* **1983**, *39*, 485. Balzani, V. *J. Chem. Ed.* **1983**, *60*, 447.

Response to "Concerning Catalysis of Photochemical Reactions"

Professor Albini's suggestion of a common effort to develop uniform terminology for catalysis in photochemistry is timely and salutary. I appreciate his initiative and the chance to respond to some questions he raises.

The recommendation that "velocity expression" rather than quantum yield be the criterion of catalysis of a photoreaction seems to me questionable. If I ask whether substance C catalyzes a photoreaction, I wish to know whether a quantity of light forms more of a certain photoproduct when C is present than when it is absent. That the velocity expression $k_r^c[C]$ is appreciable, or greater than k_r tells one nothing unless one already knows that C is a catalyst, the reason being that C could react with the substrate to give quenching or a different product. I continue to think that enhancements of quantum yields due to sensitization or enhanced intersystem crossing are best discriminated from catalysis by specifying the reactive excited state as the start of the reaction. I am skeptical that k_d can be *decreased* by an added substance without incurring a new kinetic process (and a new intermediate) which is specifiable in the quantum yield expression as a catalyst.

I agree with Professor Albini that reactivity is best expressed in terms of rate constants. However, for both ground- and excited-state reactions, catalysis can be objectively measured before one knows anything about the mechanisms of the catalyzed and uncatalyzed pathways and the operative rate constants.

I continue to find useful the analogy: rate is to rate expression as quantum yield is to quantum yield expression. Rate and quantum yield are analogous in that sense, as well as in the sense that both are the direct kinetic observables of ground- and excited-state reactions.

I did not mean to imply that *all* photoreactions can be catalyzed. As Professor Albini suggests, reactions proceeding from short-lived excited states may make catalysis unlikely—though not impossible in principle. Even more difficult to catalyze will be those photoreactions already having quantum yields of unity! We doubt that catalytic primary processes will be restricted to proton and electron transfer; a variety of hydrogen abstractions and nucleophilic and electrophilic reactions have also been shown to occur at or near the diffusion rate.

The distinction between primary and secondary steps of a photoreaction is indeed a valuable one, but even photochemists should be interested in the final photoproduct. Without such knowledge reactions cannot be specified. The secondary steps are crucial in determining what the product will be, and they are included in the quantum yield expression to the point that partitioning on the pathway ceases. The enhancement of quantum yields of products that we call catalysis is indifferent to whether the action is exerted on the excited reactant or a live intermediate. It may well be useful for classification to subdivide the phenomenon along the lines suggested by Professor Albini.

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