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W.K. WILMARTH, CHEMIST

Friends, students, colleagues of Wayne Wilmarth, and even those who had only a short acquaintanceship with him will appreciate that his contributions to chemistry are not encompassed by his publications, significant and important though their content is. Speaking for myself as a friend since we first met while graduate students at Berkeley, I have, over the entire period of our association, benefited enormously from discussions with him, whether in trying to understand the results of current research or principles which might not be even remotely related to it. On numerous occasions, not all of which I have acknowledged as meticulously as he did the benefits he derived from discussions with others, he provided the insight that led to understanding a set of puzzling observations and so opened the way to progress. Discussions with Wayne were unfailingly rewarding, rewarding not only for content—his analytical powers were great as was the store of descriptive chemistry at his command—but rewarding also because of Wayne's traits of personality: his lively interest; his discriminating enthusiasm; his ironical sense of humor moderated as it was by kindliness and understanding; and his rectitude in scientific and other matters.

Sentiments such as these, had they been voiced in Wayne's hearing, would have embarrassed him acutely. Out of respect then for what would have been his wish, I shall not dilate on them further, having already allowed myself more freedom than I ever exercised during our long friendship—respect in our relationship was tacit—and turn to an outline and critique of his research, which I can deal with more objectively than I can the more personal matters.

A bibliography covering his published work is included in the present tribute *. Simple perusal of the titles creates the impression that his work, though not large in volume, covers a very broad range of interest. The impression of breadth of interest is reinforced by a study of the papers themselves. What then further emerges is that this diversity was not achieved by his having touched lightly on a miscellany of topics, but rather through the systematic development of several major themes which embrace a wide diversity of chemical behavior. Given in the order with which I shall deal with them, and this is not necessarily the order in which his interest in them

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* References to the bibliography are identified by numbers, to other literature by letters of the alphabet.

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grew, these themes are: the basic chemistry of dihydrogen; the chemistry of binuclear complexes; reactions involving free radicals; and the mechanisms of substitution reactions. The themes were not dealt with serially, but in parallel at least to the extent that his resources allowed. These resources, as measured either by the level of outside support or by the size of his research group, were never great. Despite these limitations, he made lasting and important contributions in each of the major areas of his interest.

In several instances, his work on a topic began with a series of experiments which decisively cleared up controversy or misconceptions in the literature on a subject which had become dormant. The new insight provided by his work then sparked rapid progress in his own laboratory or those of others. This applies particularly to some aspects of the first two subjects I shall deal with. In other instances, as exemplified by the work on substitution reactions, he entered an active and already rather mature field, yet did pioneering work, improving our understanding by the judicious choice of systems for study.

THE BASIC CHEMISTRY OF DIHYDROGEN

Wilmarth's first research on the basic chemistry of dihydrogen began during his graduate work with Melvin Calvin and is the extension and culmination of preliminary studies carried out by his mentor on the oxidation of H_2 by the copper(II) salts of organic acids in quinoline or pyridine solution [A]. The net change is the reduction of Cu(II) to Cu(I) [A,10], this reaction being catalyzed by Cu(I). The form of the rate law [17,18], and the fact that para to ortho hydrogen conversion by Cu(I) takes place at the same rate as the reduction of Cu(II) [A,11] provide strong support for the mechanism which was proposed, namely that an activated complex of composition $2Cu(I) \cdot H_2$ decomposes to CuH. The reaction of H_2 with Ag^+ in the same kind of solutions yields elementary silver and involves an activated complex of composition $Ag^+ \cdot H_2$ [19]. The mechanism proposed for this reaction is heterolytic scission of the bond in H_2, producing in effect a hydride of Ag(II); it finds support in the observation that the reaction is more rapid in the presence of the anion of a weak acid than when the silver salt of an indifferent anion such as ClO_4^- is the oxidant. These studies are among the earliest definitive ones on what has become a major field in its own right, the mechanisms for the consumption or production of dihydrogen in homogeneous solution; definitive in terms of the reliability of the evidence and in terms of its cogency in supporting the mechanistic conclusions.

The remarks made in appraising the studies on dihydrogen with metal ions apply also to that now to be described, bearing on the reactions of dihydrogen acting as a Lewis acid. This phase of Wilmarth's interest in dihydrogen appears to have had its inception in a study of paramagnetic species in solution as catalysts for the conversion of para to ortho hydrogen [4], in the course of which the observation was made that solutions of metals in liquid ammonia are unexpectedly effective in bringing about the transformation. The activity was traced to adventitious amide ions, and the reaction of the base with H_2 then became the focus of study in its own right [5]. The reaction is rapid; k for the D_2–NH_3 exchange at $-53°$ is 4.9×10^3 M^{-1} s^{-1}, and shows only a small kinetic isotope effect; k for the para to ortho conversion by an analogous path is 7.7×10^3 M^{-1} s^{-1} at $-50°$ [13].

It is natural that interest in this kind of reaction would extend also to the weaker and more common base, OH^- [12]. Here, an important and controversial issue was settled by the demonstration, in support of the claim by Wirtz and Bonhoeffer [B] but challenged by others, that there is an intrinsic reaction path involving an activated complex of composition $OH^- \cdot D_2$. The most straightforward proposal for the decomposition of this activated complex was adopted, namely that the products are HOD and D^-. This finds support in the observation that para to ortho hydrogen conversion takes place at a rate which is only somewhat greater than that for exchange, as well as by studies done at very high concentration of alkali which showed that the activity coefficient of the activated complex changes in much the same way as does the activity coefficient of the alkali hydroxide itself [28]. In these reactions, the kinetic isotope effect is again very small.

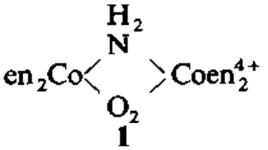
We turn now to an interest of Wilmarth's which occupied him early in his research on the basic chemistry of H_2; the catalysis by paramagnetic species in solution of the para to ortho hydrogen conversion. Because of the wide range in magnetic moment and size they feature, Wilmarth saw in the field of metal complexes [7] an opportunity to test the Wigner equation [C] which relates the rate of this conversion to molecular properties of the paramagnetic species:

$$\text{rate} \propto \mu^2/r^6$$

where μ represents the magnetic moment of the paramagnetic complex and r the separation of H_2 and the paramagnetic center. As it turned out, the research was less a test of the Wigner equation than it was a revealing study of how details of molecular shape affect the rate of encounter with a small molecule such as H_2. It is astonishing at first sight that $Cr(antipyrine)_6^{3+}$ is more effective in spin relaxation than $Cr(NH_3)_6^{3+}$, antipyrine being a much bulkier ligand than NH_3. Closer examination with the aid of molecular models shows that because NH_3 branches at the atom directly bound to the metal while antipyrine does not, it is more effectively excluded from close contact than is antipyrine. There is a great deal more to be learned from studies of this kind, extending them to other ligands, and specifically taking solvation into account, and it can only have been the lack of resources that kept Wilmarth from pursuing such a promising subject further.

BINUCLEAR COMPLEXES

Wilmarth's research on binuclear complexes, and the implications their formation has for mechanisms of redox reactions began [8] with the species



$$\mathrm{en_2Co}\left\langle\begin{matrix}\overset{\mathrm{H_2}}{\mathrm{N}}\\ \mathrm{O_2}\end{matrix}\right\rangle\mathrm{Coen_2^{4+}}$$

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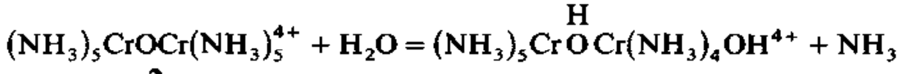
which, according to formal rules of assigning oxidation number, can be regarded as featuring a cobalt atom in the unusual 4 + oxidation state, or as now is the common practice, regarding the dioxygen unit as superoxide ion. Wilmarth chose the former assignment, but this in no way invalidates the conclusions which followed from his work. It decisively cleared up the many mysteries of the so-called isomerism which, according to the literature, the species exhibits. The mystery begins with the preparative procedures: when the product solution, which itself is red, is acidified by the slow addition of dilute nitric acid, a red solid results, but when concentrated nitric acid is used, the solid is green. The interconversions which were reported in the early literature are equally puzzling, at least when they are viewed as isomeric transformations. One of the basic principles which William C. Bray inculcated in students in Chemistry 120 at Berkeley was that an understanding of a reaction system begins with stoichiometry. This durable principle was repeatedly put to good use by Wilmarth, in this instance by showing that the red and green forms are in fact not isomeric, but are connected by the redox change:

$$\text{green} + \mathrm{H^+} + \mathrm{e^-} = \text{red}$$

Formula **1** applies to the green species, the red differing from it in composition by having one atom of hydrogen more. Only the green form is paramagnetic. The puzzling observation that OH^- converts the green species to the red was rendered less so by the later observation [35] that the transformation is not quantitative and that some ligand, presumably NH_3, is sacrificed to oxidation. But how can the fact that bromide ion, which by no stretch of the imagination can act as an oxidizing agent, produces the green, or oxidized form, from the red be understood? This too was divested of mystery, proof being offered that Br^- catalyzes the disproportionation of the red species; in terms of current usage in assigning oxidation states, peroxide disproportionates to O_2^- and OH^-. The clarification of the remarkable chemistry of this system set the stage for further progress by others, where the nature of the protonation of the red form was more completely elaborated, and the chemistry of cobalt(III) peroxo and superoxo complexes greatly expanded [D].

The literature on the rhodo and erythro forms of a binuclear chromium(III) ammine was as puzzling as that of the presumed isomeric forms of **1**, and clarification by Wilmarth et al. [20] of the issues in this system followed the general lines of that just described. In this case as well, what had been considered to be an isomeric change proved to be a change in composition: the conversion in basic solution of the rhodo species to the erythro was shown to involve aquation



$$\underset{\mathbf{2}}{(NH_3)_5CrOCr(NH_3)_5^{4+}} + H_2O = \underset{\mathbf{3}}{(NH_3)_5Cr\overset{H}{O}Cr(NH_3)_4OH^{4+}} + NH_3$$

Left to explain was the earlier claim that the erythro species can be reconverted to the rhodo by heating a salt containing it at 100°; here it was shown that while the reported conversion does take place, it is not quantitative, and thus no conservation laws are violated. Much work has subsequently been done on this system—one of the points of special interest is that the high lability is restricted to a single one of the pair of chromium(III) centers—without any of the essential conclusions reached by Wilmarth et al. being challenged. In referring to Wilmarth's study in the course of introducing his own research on the system, Schwarzenbach [E] wrote "Mit diesen neuen Befunden konnten nun alle Bescheinungen gedeutet werden".

Wilmarth's interest then turned to exploiting the substitution inertia of certain binuclear species resulting from redox processes, to probe the mechanisms of their formation. In the course of this work, the new binuclear species, $[(NC)_5CoO_2Co(CN)_5]^{6-}$ and $[(NC)_5FeCNCo(CN)_5]^{6-}$, as well as the $1e^-$ oxidation products of each, were prepared [26]. These molecules are interesting in their own right, the former adding to the class of μ-peroxo and μ-superoxo species, and the second heralding the subject of mixed valence molecules; moreover, their formation as the products of oxidation of $Co(CN)_5^{3-}$ by $Fe(CN)_6^{3-}$ and O_2, respectively, demonstrated inner-sphere mechanisms for the two reactions. There is a significant contrast between the way $Cr(CN)_5^{3-}$ and $Co(CN)_5^{3-}$ (it is understood that excess CN is present) react with O_2, the former yielding $Cr(CN)_6^{3-}$, thus indicating an outer-sphere mechanism. This contrast is maintained in the reactions of the two reducing agents with H_2O_2, where $Cr(CN)_6^{3-}$ and $Co(CN)_5H_2O^{2-}$ are the respective products.

The mechanism of the reaction of O_2 with Cr(II) was also explored by oxygen isotopic tracer methods [27]. In strongly ammoniacal solution the rhodo complex (2) is formed by the reaction of Cr(II) with O_2. Over a rather wide range of conditions, ca. 50% of this product is found to derive its oxygen atom content from $\otimes_2$. To explain the tracer result, Wilmarth et al. invoked Cr(IV) as an intermediate, as well as its expected substitution lability [F]. They proposed that $[(NH_3)_5Cr\otimes\otimes Cr(NH_3)_5]^{4+}$ is produced in the first stage of the reaction, and that this species reacts with $Cr(NH_3)_5^{2+}$ to produce labelled rhodo ion. Although labelled Cr(IV) would also result, it is not unreasonable to suppose, as the authors suggest, that this undergoes exchange with solvent before it is converted by $Cr(NH_3)_5^{2+}$ to a second molecule of the rhodo ion.

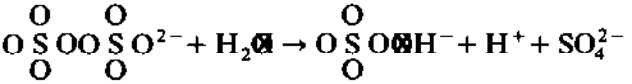
REACTIONS INVOLVING FREE RADICALS

Apart from one paper devoted to the chemistry of a free radical species at the preparative level (tri-α-naphthylboron monoanion in tetrahydrofuran) [23], Wilmarth's work in this field was devoted to their reactions, in many cases in systems in which the concentrations are so low as to preclude convincing characterization by physicochemical methods. His first effort [9], devoted to the reactions of free radicals, was an examination of the applicability in that context of the Hammett equation. On the one hand it had been shown that the rates of dissociation of hexaphenylethane are not correlated by the equation, but that on the other [G] the rates of dissociation of benzoyl peroxides are. Wilmarth's early motivation for working on this subject is best described in his own words: "Since the only successful application of the equation involves the calculation of rate constants, a correlation of dissociation constants in even a single instance would strengthen the probability that the equation was of some general validity". Schwartz and Wilmarth [9] showed that the data of Goldschmidt [H] on the dissociation of tetrazanes to hydrazyl radicals conform to a Hammett plot. The data themselves were refined in a later study [14], which eliminated the need to allow for the effects of changing the solvent, and in which the effect of temperature was dealt with. The work was then extended to include the rates of dissociation [15]. The differences in the behavior of the different systems can be understood when account is taken of changes in the extent of electron delocalization on the formation of the free radical species.

A paper on the photolysis of $S_2O_8^{2-}$ in aqueous solution [21] introduces a new phase of Wilmarth's work on free radicals, the interest now shifting to the chemistry of highly reactive inorganic radical species. In the paper under consideration, it centers on SO_4^-, but as we shall see, this work led naturally to a curiosity about other important inorganic radical intermediates. Two reaction paths for the photochemical decomposition of $S_2O_8^{2-}$ to SO_4^{2-} and O_2 were uncovered, the bifurcation being ascribed to different modes of decomposition of the photo-activated molecule. In reaction by the major path which accounts for 0.8 of the events, it is assumed that this decomposition produces SO_4^-. Reaction by this path is inhibited by HSO_4^-, in consonance with the assumption of the equilibrium process:

$$SO_4^- + H_2\otimes = H\otimes + H^+ + SO_4^{2-} \qquad (1)$$

Tracer studies showed that the oxygen produced by this path has the isotopic content of the solvent. Moreover, isotopic exchange between SO_4^{2-} and $S_2O_8^{2-}$ accompanies reaction by the major path, an observation which is easily accommodated by equilibrium 1. The oxygen liberated by the minor reaction path is derived partly from $S_2O_8^{2-}$, and in this instance, polar cleavage of the excited reactant is postulated:



$$O\overset{O}{\underset{O}{S}}OO\overset{O}{\underset{O}{S}}O^{2-} + H_2\otimes \rightarrow O\overset{O}{\underset{O}{S}}O\otimes H^- + H^+ + SO_4^{2-}$$

Eventual oxidation of the permonosulfate ion then leads to the formation of $O\otimes$ by sulfur–oxygen bond scission.

The reaction of SO_4^- with H_2O is also a key step in the isotopic exchange between O_2 and aqueous alkali as induced by the decomposition of $S_2O_8^{2-}$ [22]. The extent of exchange is small in acidic solution but rises sharply when the pH becomes greater than 11. A similar effect is observed in the chain reaction of H_2 with $S_2O_8^{2-}$, in which hydroxyl radical is implicated, and had been reported also for exchange induced by high energy radiation acting on aqueous solution [I]. The rises imply that O^- is a more effective catalyst for the exchange than is HO, but in analyzing the data, Wilmarth avoided the trap that others [J] have fallen into of equating such a rise with a pK_a value, and recognized that the rise reflects the value of pK_a biased by a ratio of rate constants.

In a continuation of the investigation of $S_2O_8^{2-}$, its reaction with H_2O_2 was studied [24]. This work provides a good textbook example of how the rate law for a chain reaction changes with the nature of the chain breaking step, the rate law responding to changes in the ratios of the concentrations of the bulk reagents, and in some cases, to the concentrations themselves. A subsequent study [32] was devoted to the concentration regime in which the consumption of H_2O_2 exceeds that of $S_2O_8^{2-}$. The excess consumption of H_2O_2 is ascribable to the reaction of HO_2 with H_2O_2, and it is a function of the relative rates of reaction of HO_2 with H_2O_2 and $S_2O_8^{2-}$. These relative rates are affected by pH, but as in the system just described, an equilibrium dissociation constant, that of HO_2 in this case, is not fixed by the data but rather the dissociation constant multiplied by a ratio of specific rates. The value of K_{HO_2} having since been determined [K], Wilmarth's data can be used to calculate the relative specific rate for the reaction of H_2O_2 with O_2^- and HO_2.

Wilmarth's attention turned next to the photolysis of H_2O_2 and the oxidation of CO induced thereby [33]. An important general conclusion from the work is that $H_2O + O$ are not, as suggested by Hunt and Taube [L], the products which escape cage recombination, but rather that this product is HO. A more specific but nevertheless important result is that the relative rate of reaction of HO with H_2O_2 and CO was determined (72 ± 4) [33]. The importance of a result such as this is that the reactivity ratio is a property of the radical which can be used to characterize it in other systems in which it is assumed to be an intermediate. Prior to this rather direct determination of the reactivity ratio, it could only be deduced from a series of reactivity ratios. The reasonable agreement between the two values confirms the validity of the individual reactivity ratios comprising the series.

The interest in the reactions of $S_2O_8^{2-}$ led to an excellent general article on the reaction mechanisms of $S_2O_8^{2-}$ in aqueous solution [25]. It reflects the results of careful reading of the literature, good organization and incisive critical analysis. Credit for the quality of the article must of course be shared with the co-author, credit which Wilmarth freely acknowledged in the discussions I had with him about the paper.

The work which seemed to become Wilmarth's major concern towards the end of his career, as is represented by an earlier paper with Stanbury [48], and three papers appearing in this volume, can be viewed as a direct outgrowth of his researches on free radical chemistry. Most inorganic chemists concerned with basic aspects of electron transfer reactions restricted their interest to transition metal complexes. Wilmarth appreciated the need to extend the investigations to molecules of the main group elements. It is clear from the papers referred to that this is a very productive and important area for investigation. Effects are encountered which are outside the regime which the Marcus correlation, so useful for many electron transfer reactions of metal complexes, was designed to cover. They include reactions partly governed by diffusion control and possibly some which fail to meet the weak overlap criterion [M].

THE MECHANISM OF SUBSTITUTION REACTIONS

Wilmarth devoted more effort to this topic than any of the others I have dealt with. If the space I accord to it does not reflect his own emphasis, it should not be taken to indicate that I think less highly of this work than I do of that done on the other major topics. It does reflect the fact that because this work is more recent, and represents what was a mainline interest of many physical inorganic chemists, it is better known than some of his earlier efforts. In addition, it is covered in an excellent review with Byrd as co-author [46], and is, as well, represented in several papers appearing for the first time in this volume.

It is well known that the rate law characteristic of an S_N2 substitution reaction can also be interpreted as an S_N1 process, at least when, as is usually the case in aqueous solution, the solvent intervenes in the substitution reaction. On the other hand, kinetic evidence alone can often provide unambiguous evidence for an S_N1 process even when the solvent intervenes. When in producing a complex from an aquo ion, the rate becomes independent both of the concentration and identity of the entering ligand, we are quite certain that an intermediate is being produced which owes nothing to the character of the entering group; this intermediate can usually be taken to be a species of reduced coordination number as compared to the reactant. Wilmarth concentrated his effort on systems which showed promise of conforming to the S_N1 mechanistic limit.

Some of the early work devoted to the mechanism of substitution in complex ions involved reactions of cationic complexes with anionic ligands. In such systems, evidence of rate saturation as the ligand concentration increases is often encountered, and, in extreme cases, as for example in the reaction of $Co(NH_3)_5H_2O^{3+}$ with SO_4^{2-} [N], the rate can become independent of the concentration of the entering group. The kinetic evidence in this particular system and other similar systems, however, only shows that there is significant outer-sphere association of the reagents. If kinetic evidence for an S_N1 process is to be obtained, outer-sphere association of the reagents must be avoided. This was achieved by Wilmarth in the first series of studies on this subject, choosing an anionic metal complex, $Co(CN)_5OH_2^{2-}$, reacting with anions as entering ligands. The strategy adopted in these studies was impeccable, but as acknowledged by Haim in his recent report [O] on a reexamination of one of the systems, the evidence (rate saturation at high ligand concentration) which supported the conclusion that there is a common intermediate for different entering ligands was flawed because of an impurity.

An alternative strategy for favoring the S_N1 limit is to study complexes which contain labilizing ligands. Effects of this kind, known for many years and well documented for substitution in complexes of Pt(II), have been much less systematically explored for octahedral complexes.

In the first of a series of papers devoted to sulfito complexes of Co(III), the great labilizing influence of one sulfite on another *trans* to it in $Co(CN)_4(SO_3)_2^{5-}$ is noted. The main focus in this study was to determine some of the basic properties of the mono and the bis sulfito complexes, such as the lability of the sulfito groups themselves, the affinities of the species for protons, and to establish the *trans* configuration for the bis-sulfito species, as preparation for a study of the rates of substitution in $Co(CN)_4(SO_3)OH_2^{3-}$. In this paper [36], unpublished studies by Chen on the rate of ligation for $Co(CN)_4SO_3OH_2^{3-}$ are referred to, which generalize the *trans* labilizing effect of SO_3^{2-}. It is an additional step to show that this labilization leads to the formation of an intermediate, the mechanism for substitution then conforming to the S_N1 limit. This step was taken by Halpern and co-workers [P] for SO_3^{2-} labilizing the position *trans* to it on Co(III) with ammonia as the auxiliary ligand. In the second paper from Wilmarth's laboratory on SO_3^{2-} as a labilizing group, the kinetic data for CN^- acting on $Co(CN)_4(SO_3)H_2O^{3-}$ are reported [37] and are shown to conform to a limiting S_N1 mechanism. The system is complicated by the fact that Co(III) is distributed between the aquo and the hydroxo species. At high concentration of CN^-, the rate becomes independent of its concentration, and the rate determining step is the loss of water from $Co(CN)_4SO_3OH_2^{3-}$. The authors point out that the intermediate $Co(CN)_4SO_3^{3-}$ may in fact be hexacoordinated, with SO_3^{2-} acting as a bidentate ligand.

The last of the papers exploring the sulfito series, apart from those appearing in this volume, describe substitution by various nucleophiles in *trans*-sulfitoaquo-bis(dimethylglyoximato) [42] cobalt(III). A remarkable finding is that while with SO_3^{2-} as entering group, rate saturation is observed, with thiourea, N_3^-, I^-, pyridine, thiosulfate, and even HSO_3^-, there is no evidence for such an effect, and the rate with these ligands can greatly exceed the limit observed with SO_3^{2-}. It was concluded from these results that the path involving bond making in the activated complex by SO_3^{2-} is unimportant compared with that involving an intermediate derived from the Co(III) complex by loss of water. What is puzzling is that the other entering groups mentioned totally disregard the intermediate, as evidenced by the fact that the rates are strictly first order in the entering group. Evidence for the dual path behavior is recorded for NCS^- but the analysis of the data for this system does not yield an independent value of the limiting S_N1 rate. Thus it is possible that some kind of association between the cobalt(III) complex and SO_3^{2-} and NCS^-, rather than the intervention of a distinct S_N1 path, is responsible for the kinetic behavior.

The last paper of the series on substitution to be commented on here involves substitution on alkylbis(dimethylglyoxamato)aquocobalt(III). This study, because of its novelty and the growing interest in related molecules of biological interest, was published as a "Communication" [45]. It is an excellent contribution and can be taken as a model for what a "Communication" in an area such as this should contain. Enough data are given to satisfy the reader that the authors were fully in control of the systems. Furthermore, the experimental effort was not limited to the study of rates but relevant equilibrium data were also reported. This feature of Wilmarth's work on substitution reaction has not been sufficiently stressed in my account. He was always alert to the need to be concerned about the equilibrium state as important in its own right, and of course as essential for the interpretation of the kinetic data, and where reversibility was featured, it was fully investigated.

CODA

There is a hiatus in Wilmarth's publication record beginning in 1971. Underlying this was his failure to win outside support for his research, a disappointment which may have aggravated a physical condition of his. He had a vital, even consuming interest in research, and his disappointment was a reaction less to the way the decisions on his proposal may have reflected on the quality of his past work, than of frustration he felt because they limited his ability to pursue his interests in research. In view of Wilmarth's distinguished record of achievement, I still find it astonishing that he was denied continued support. No system of rating proposals will ever be perfect, but under any system there will be cases of injustice so grave as to remind us that we must continually think about how the system can be improved. In my view, Wilmarth's is such a case. Though his work towards the end of his career may not have been at the height of current fashion, an objective examination of what he was trying to do could hardly have led to the conclusion that it was trivial. The reactivities of inorganic free radicals are poorly understood. This is equally true of the reactivity patterns he was investigating in substitution reactions. Few, if any, were doing better work in these areas than he was.

Something also needs to be said about Wilmarth as a teacher, particularly because the role of his co-workers has not been emphasized in my account. Work of the quality that was done would only have been possible if harmonious relations between him and his co-workers prevailed. His standards were exacting, and harmony in that situation is possible only if the co-workers respect their mentor. It has been my pleasure to have had a close association with two of Wilmarth's co-workers. Both from the beginning of our association showed evidence of superb training in scientific investigation, whether in planning, experimentation or thinking about research. Both are gifted, so that Wilmarth's seeds of wisdom fell on fertile ground.

Henry Taube
Palo Alto, California
January, 1983

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