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Organic Molecules as Bridging Groups in Electron-Transfer Reactions

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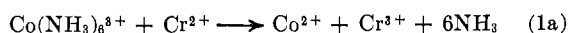
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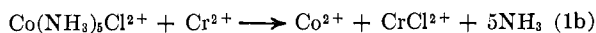
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This Account deals with electron-transfer (redox) reactions between two metal centers and is confined to changes of one oxidation unit. Prototypes of the two broad classes of such reactions are reactions 1a and 1b, which, formally, have much in common.

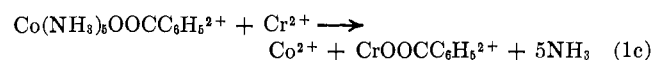


(Electron transfer, *outer-sphere* path; $k = 10^{-4} M^{-1} \text{sec}^{-1}$.)



(Electron and ligand transfer, *inner-sphere* or *bridge* path; $k = 6 \times 10^5 M^{-1} \text{sec}^{-1}$.)

Note that replacement of only one of the six cobalt-bound NH_3 ligands in (1a) with chloride accelerates the reaction by a factor of over 10^9 and, moreover, changes its essential nature. In (1a) the redox reaction takes place without alteration of the ligand environment of either metal (the ammonia molecules are known to be lost from $\text{Co}(\text{II})$ after electron transfer has occurred). In contrast, reduction of the chloro complex (1b) is accompanied by transfer of chlorine from cobalt(III) to chromium; with every act of electron transfer there is an act of ligand transfer, and at no point in the reaction is the chloride free from the coordination sphere of both metal centers.¹ We thus refer to chloride in this reaction as a *bridging* or *mediating* group.



(*Inner sphere* or *bridge* path; $k = 0.15 M^{-1} \text{sec}^{-1}$.)

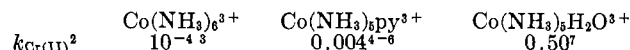
Reaction 1c moves the discussion into the realm of organic chemistry. The bridging benzoato group, like the chloride in (1b), is transferred from oxidant to reductant but differs from chloride in having two different atoms (the two oxygens) that could possibly accommodate the $\text{Cr}(\text{II})$.

During the 1960's, electron-transfer reactions involving bridging action by almost 200 different organic

(1) (a) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953); (b) H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

ligands have been examined, and it has been found possible, by suitable modification of such mediating groups, to change redox rates by more than eight orders of magnitude. This wide variation naturally prompts the question as to what factors govern the effectiveness of such groups, and enough data are at hand at least to point the directions in which answers lie.

How does mediation occur? Certainly the bridging ligand must be able to function as a Lewis base toward both metal centers, for it is initially bound to one of the metal ions and must penetrate the coordination sphere of the reaction partner, forming a *binuclear intermediate* or *precursor complex*, before the act of electron transfer takes place. Consider the series



Of these three, only the aquo complex is reduced with ligand transfer, for only in this complex is there an unshared electron pair free to interact with the reducing center. The π electrons in the pyridine complex are evidently not very effective in bridging. There is no indication that a chromium-bound pyridine complex intervenes here, but the possibility is not excluded that the π electrons are somehow involved in electron mediation.

Broadly speaking, there are two ways in which variations in the bridging ligand may influence the redox process. Such variation may affect the stability of the precursor complex, it may alter the rate of electron migration within the complex, or it may do both. There are a number of instances in which differences in observed rates are far too great to be attributed to differences in the concentrations of precursor complexes.

(2) Specific rates for reduction with $\text{Cr}(\text{II})$; second-order specific rates in this Account are quoted in $M^{-1} \text{sec}^{-1}$; conditions, unless otherwise stated, are unit ionic strength, 25°.

(3) A. M. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

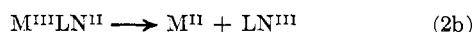
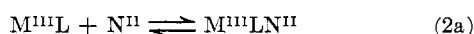
(4) A. M. Sargeson and R. B. Jordan, *Inorg. Chem.*, **5**, 1091 (1966).

(5) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965).

(6) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

(7) A. M. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

Electron transfer *via* an inner-sphere path is often separated into steps, *e.g.*, (2a) and (2b), where substi-

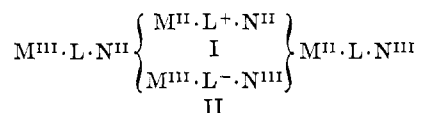


tution on N^{II} is taken to be much more rapid than that on M^{III} . It is acknowledged that in comparing rates we must consider the net activation process, reaction 3,



and the energy for this is independent of the position of the equilibrium in (2a) provided that this equilibrium does not deplete the reactants. Nevertheless, the division into steps is useful, for if rate differences merely reflect differences in stabilities of the precursor complexes, it would be idle to discuss other effects. Such a separation, moreover, seems realistic except in reactions where formation of precursor complexes is rate determining. Such cases have been encountered^{8,9} in some reactions of $V(H_2O)_6^{2+}$, which undergoes substitution slowly,¹⁰ but are not to be expected for $Cr(H_2O)_6^{2+}$ (which undergoes substitution very rapidly¹¹) except possibly in its most rapid oxidations (with specific rates much greater than $10^6 M^{-1} sec^{-1}$).

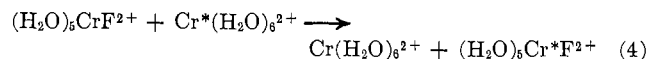
Mechanism of Electron Transfer for a Simple Bridging Group. Apart from considerations of the stability of precursor complexes, an understanding of rate behavior centers on the mechanism of electron transfer through the bridge. Such mechanisms have been considered in general terms by George and Griffith,¹² by Halpern and Orgel,¹³ and, earlier, as applied to single ions in a solid, by Zener.¹⁴ Of the several alternative mechanisms the most clearly defined and that which appears to be the most readily verifiable is the chemical mechanism.¹² Here the precursor complex (*cf.* eq 2a) is considered to be activated to a configuration in which the bridging ligand is either oxidized by one or reduced by the other associated ion, the



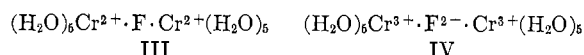
reaction then being completed when the electron hole (alternative I) or the excess electron (alternative II) is passed on to the complementary agent. If the intermediate radical states I and II last long enough, their energies will be well-defined, though these energies may still be difficult to calculate from known properties of the partners. Only when the uncertainty broadening

is small may we consider a chemical mechanism as distinct from some of the alternatives, and, in seeking for evidence of the chemical mechanism, we will have in mind states of narrowly defined energy for the intermediates I and II. For the time being, only gross effects are being considered, and it is, therefore, unnecessary to offer a quantitative definition of what is meant by a "well-defined" energy. Where the distinction is important, we will be concerned with evidence that certain systems do conform to the behavior expected in the limit of a true radical-ion mechanism.

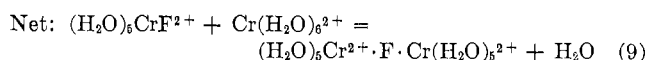
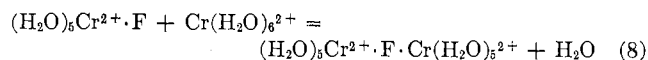
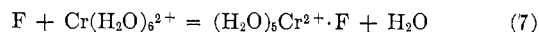
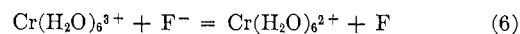
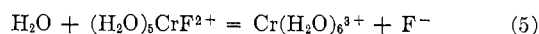
It is next helpful to consider the problem of mechanism for a simple system, choosing one in which energetics allow us to reject the chemical mechanism. Reaction 4 has a rate constant¹⁵ of $2.2 \times 10^{-2} M^{-1} sec^{-1}$.



If the reaction were to take place by the chemical mechanism, then the system would be required to pass through either III or IV. The net activation process

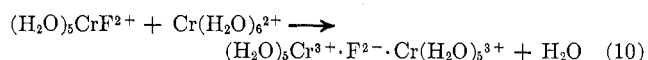


to achieve state III is the sum of steps 5-9. Steps 5

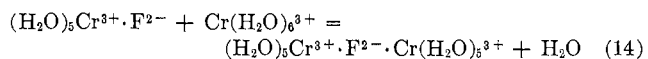
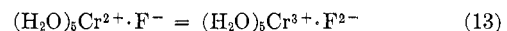
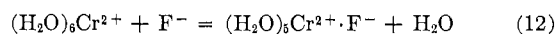
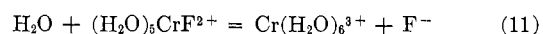


and 6 have ΔF° values of 6¹⁶ and 104¹⁷ kcal, respectively. There is little, if any, compensation for this energy cost in reactions 7 and 8 in which F, a poor nucleophile, replaces H_2O from the coordination sphere of Cr^{2+} . ΔF° for the net activation process is, therefore, about 100 kcal, far in excess of ΔF^\ddagger .

The net activation process corresponding to intermediate state IV is given by eq 10, and an approximate



ΔF° for this reaction emerges from the cycle 11-13.



Reaction 12 has a value of ΔF° which is only slightly negative. That for reaction 11 has already been commented on. Reaction 14 probably has a favorable standard free-energy change, but it will do little more than compensate for reaction 11. The important energy term is that contributed by reaction 13. This en-

(8) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

(9) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(10) *k* for the process $(H_2O)_5V^{2+} + (H_2O) = (H_2O)_6V^{2+} + (H_2O)^*$ at 25° is $90 M sec^{-1}$: M. V. Olson, Y. Kanizawa, and H. Taube, *J. Chem. Phys.*, in press.

(11) *k* for the analogous process with Cr^{2+} is greater than $10^9 sec^{-1}$: C. W. Merideth, Ph.D. Thesis, University of California, Berkeley, 1966.

(12) P. George and J. Griffith, *Enzymes*, **1**, 347 (1959).

(13) J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960).

(14) C. Zener, *Phys. Rev.*, **82**, 403 (1951).

(15) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(16) A. S. Wilson and H. Taube, *ibid.*, **74**, 3509 (1952).

(17) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., Englewood Cliffs, N. J., 1952.

Table I
Comparisons of Rates of Reduction by Cr²⁺ of Carboxylatopentaamminecobalt(III) Complexes

	k_0 at 25° and $\mu = 1.0^a$	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
HCOO ⁻	7.2 (7), ^b (0.13) ^c	8.3	-27
CH ₃ COO ⁻	0.35 (0.18) ^d	8.2	-33
(CH ₃) ₂ CCOO ⁻	9.6 × 10 ⁻³ (8.8 × 10 ⁻³) ^e	11.1	-31
CF ₃ COO ⁻	0.017 (at $\mu = 0.2$)	9.3	-35
C ₆ H ₅ COO ⁻	0.15 (0.14) ^f	9.0	-33
CH ₂ NH ₃ ⁺ COO ⁻	(0.060), ^g (0.06), ^h (0.53) ⁱ	7.7	-38
CH ₂ OHCOO ⁻	(3.1), ^b (0.60 + $\frac{0.31}{(H^+)}$) ^j	9.0	-26

^a Values from ref 24 except those in parentheses. Where there is substantial disagreement, the value given first is the preferred one. ^b R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, **87**, 5597 (1965). ^c R. T. M. Fraser, "Proceedings of the 8th International Conference on Coordination Chemistry," V. Gutmann, Ed., Springer, Vienna, 1964, p 268. ^d D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961). ^e E. S. Gould, *ibid.*, **88**, 2983 (1966). ^f R. T. M. Fraser, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N.Y., 1961, pp 187-195. ^g R. Holwerda, E. Deutsch, and H. Taube, to be published. ^h K. D. Kopple and G. F. Svatos, *J. Am. Chem. Soc.*, **82**, 3227 (1960). ⁱ R. T. M. Fraser, *Inorg. Chem.*, **3**, 1501 (1964).

ergy could be estimated from the onset of charge-transfer absorption in the fluoride complex of Cr²⁺ if the measurements were at hand. Failing this, we can use the onset of charge-transfer absorption in Cr-(H₂O)₆²⁺ as a lower limit of the energy cost of reaction 13. The charge-transfer absorption begins in the ultraviolet region,¹⁸ and thus we conclude that ΔF° for reaction 10 is greater than about 70 kcal, eliminating any hope of accounting for electron transfer in reaction 4 by this means.

It is much easier to eliminate a particular mechanism than to describe how the change in oxidation state does take place. The mechanism can probably usefully be considered to involve resonance transfer of an electron from Cr²⁺ to Cr³⁺, but conceding this still leaves obscure the energy state of the system as the electron is being redistributed and the contributions to the wave function for this state of the various orbitals of the metal ions and the bridging groups.

Organic Ligands in Oxidizing Complexes. Before detailed comparisons of different organic ligands as bridging groups are made, a general comment concerning the nature of the complexes is in order. Thus far, the most convincing mechanistic information has emerged from studies in which the oxidizing complex undergoes substitution very slowly, and it is further useful if the reductant yields, on oxidation, a complex which is likewise substitution inert. The evidence on mechanisms is particularly direct with complexes in which NH₃ is used as "blocking" group, *i.e.*, as a group which cannot bridge (NH₃ has no low-lying unoccupied orbitals, and, when coordinated, lacks unshared electron pairs to engage the partner reaction cation).

The complexes of Co(III), Cr(III), and Ru(III) have been the most investigated as oxidants. As to ligands, we now pay special attention to the "lead-in" atoms, namely those atoms which provide attachment of the ligands to the oxidizing metal centers. Thus far only O and N have been used as lead-in atoms. Of the oxygen derivatives, only carboxylates have been extensively studied. Numerous alcohol complexes of Co-

(III),⁴ Cr(III),¹⁹ and Ru(III) can be expected to be kinetically stable, but aldehyde or ketone complexes are likely to prove intractable because of rapid aquation²⁰ (probably by C-O bond scission). Of the numerous ligand possibilities which can be considered for nitrogen as lead-in atom, only the heterocyclic derivatives have been at all intensively investigated as bridging groups in electron-transfer reactions. Among the nitrogen derivatives, abundant opportunities remain to be exploited. Many organic amines are nucleophilic enough to ensure that complexes with Co(III), Cr(III), and Ru(III) are kinetically stable, including, presumably, nitrogen-bound amino acid complexes, but these may be no more interesting than ammonia complexes for present purposes. Nitrile complexes of Co(III)⁴ and Ru(III)²¹ have been shown to be kinetically stable, as have several N-bound amide complexes. Virtually nothing has been done with ligands having S as lead-in atom except for NCS⁻, and preparative chemistry with the ligands of this important class is needed. Finally, attention is directed to the category of ligands with carbon as lead-in atom. Several complexes with (H₂O)₅Cr³⁺ are known,²² and this class can undoubtedly be extended to include also other metal ion centers.

Influence on Rates of Steric, Inductive, and Chelation Effects. The emphasis in this article centers on ligands with conjugated bond systems, using effects observed with such groups to arrive at an understanding of the mechanism of electron transfer in these cases. However, it is difficult to avoid contributions also of steric, inductive, and other interactions. Accordingly, some comparisons²³ are presented in Table I which are useful in assessing the sensitivity of the rates to these influences.

First, what of the structure of the activated complex? With the possible exception of the pivalato

(19) R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964); D. N. Kemp and E. L. King, *ibid.*, **89**, 3433 (1967).

(20) Unpublished experiments by F. Nordmeyer have shown that [(NH₃)₅CoOC(CH₃)₂]³⁺ is transformed to (NH₃)₅CoOH₂³⁺ in less than 1 min in water at room temperature.

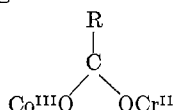
(21) P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968).

(22) (a) F. A. L. Anet and E. LeBlanc, *J. Am. Chem. Soc.*, **79**, 2649 (1957); (b) J. K. Kochi and P. E. Mocado, *ibid.*, **88**, 4094 (1966).

(18) F. S. Dainton, Special Publication No. 1, The Chemical Society, London, 1954, p 18.

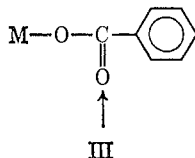
system, ligand transfer is essentially complete in every case,^{24a} proving that Cr^{2+} attacks one of the two oxygens of the carboxylate, but not telling us which. There is good evidence,^{24b} based on the aquation behavior of the binuclear complexes $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{O}_2\text{CHCr}^{\text{III}}$ and $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{OOCCH}_2\text{Cr}^{\text{III}}$, formed on the reduction by Cr^{2+} of the corresponding Ru(III) complexes, that Ru and Cr occupy separate oxygen atoms, and we infer, therefore, that Cr^{2+} attacks the carbonyl rather than the lead-in oxygen of the carboxylate in the Ru(III) complexes. The rate pattern for the reduction by Cr^{2+} of the carboxylatopentaamminecobalt(III) complexes is remarkably like that for the reduction of the analogous Ru(III) species, and it is probable, but not certain, that the activated complexes have similar structures.

The kinetic consequences of steric repulsion are evident from the first three entries of Table I. Experiments with molecular models constructed to conform to the geometry suggested for the activated complex in-

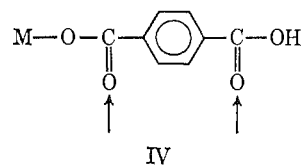


dicates that when at least one hydrogen atom is retained in the α position, a configuration can be found in which approach of $\text{Cr}(\text{H}_2\text{O})_5$ is not severely hindered. Inductive effects appear to be quite small, as indicated by comparing entries 2 and 4 of the table. The entry for glycolate as ligand compared to acetate gives a measure of the accelerating effect of the important complexing function OH when it is in a good position for chelation with the reducing agent. The three effects mentioned, as well as that produced by an increase in positive charge (glycinate as ligand), appear to reflect merely the manner in which the ligands affect the concentrations of the precursor binuclear complexes. That is, it seems likely that if the concentrations of these binuclear complexes were measured, these would closely parallel the rate variations shown in Table I.

Introduction of Ligands with Conjugated Bond Systems. In considering the ligands which feature extended conjugate bond systems in a purely formal way, two classes can be distinguished. One such class is exemplified by benzoate ion; here the extended conjugated bond system is pendant to the bond system carrying the electron from reducing agent to oxidizing agent.



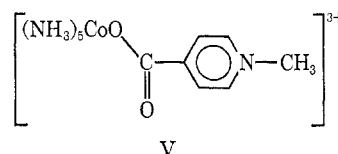
The other class is exemplified by terephthalate; here attack by the reducing agent is possible in the same way as on benzoate, that is, on the metal-bound carboxyl, but



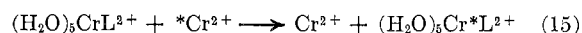
it is conceivable that the reductant may attack the unbound "remote" carboxyl, with the electron moving through the conjugated bond system to the oxidizing metal center, M.

Pendant Groups Affecting Rate of Electron Transfer.

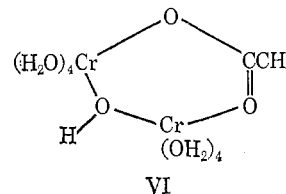
The entry for benzoate in Table I provides no hint that pendant groups can influence the rate of electron transfer, but other data do demonstrate pendant group effects. The complex V in its steric environment in the vicinity



of the bound carboxyl group closely resembles the benzoate; if anything, because of the positive charge on nitrogen, a lower concentration of precursor complex is expected than for the benzoate complex. Complex V, however, is reduced about nine times as rapidly as the benzoate.²⁵ More strikingly, the glycolato complex (Table I, $k_0 = 3.1$) is reduced much more slowly than the glyoxylato²⁶ complex ($k_0 > 7 \times 10^3$) although the α carbonyl group should be less effective in binding Cr^{2+} in the precursor complex than is the α hydroxyl. Perhaps the most striking pendant group effect has been encountered in reaction 15, with $\text{L} =$ acetate or the acid



fumarate anion. In the acetato system,²⁷ k_{-h} is observed to be $5.8 \times 10^{-4} \text{ sec}^{-1}$ and $k_0 > 6 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$; in the fumarato system,²⁸ k_{-h} is 0.70 (at 10°) and k_0 is 1.7 (at 10°). In the acetato case, the most reasonable structure for the activated complex operating in reaction by the k_{-h} path is VI, and it is likely that the acti-



(23) The general rate law for the reactions to be discussed takes the form

$$-d(\text{Cr}^{2+})/dt = -d(\text{Ox})/dt = (\text{Cr}^{2+})(\text{Ox})[k_{-h}/(\text{H}^+) + k_0 + k_h(\text{H}^+)]$$

Not all paths are observed in all the systems.

(24) (a) M. Barrett, Ph.D. Thesis, Stanford University, 1967. In several cases, the new rate measurements require substantial revision of earlier values. (b) J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

(25) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **85**, 3706 (1963).

(26) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(27) E. Deutsch and H. Taube, *ibid.*, **7**, 1532 (1968).

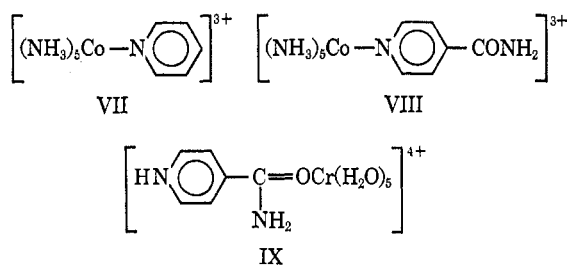
(28) H. Diaz, work in progress.

the ratio of the specific rates for the two processes $(\text{H}_2\text{O})_4\text{CrOHL}^+ + \text{Cr}^{2+} \rightarrow$ will be almost the same as the ratios of the observed values of k_{-h} . Thus, a powerful influence of a group such as $-\text{CH}=\text{CHCO}_2\text{H}$ replacing CH_3 is revealed, even though the group is not in the direct line of electron transfer.

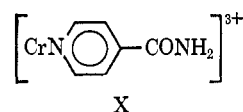
It has been suggested^{25,26,29} that the improvement of $\text{N-CH}_3\text{C}_5\text{H}_4\text{NCOO}^-$ (N-methylpyridine-4-carboxylate) over $\text{C}_6\text{H}_5\text{COO}^-$, and of HCOCOO^- over CH_3COO^- , as mediators in electron transfer is associated with the fact that the first member of each pair has an unoccupied orbital lying at lower energy. The greater accessibility of the orbital is, in a loose way at least, related to the easier reducibility of the species. This correlation can be extended to the acetato-fumarato comparison, but an explanation for the correlation has yet to be suggested; this will be discussed further below.

Electron Transfer by Remote Attack. In earlier examples the characterization of intermediate Cr(III) products provided evidence on the question of where $\text{Cr}^{2+}(\text{aq})$ attacks the carboxylate cobalt(III) complexes. A like strategy is applicable to diagnosing remote attack in certain systems when these are suitably chosen. In particular, a bridging ligand should lead to different products depending on where Cr^{2+} attacks the oxidizing complex. It is clear that symmetrical ligands such as the fumarate or terephthalate ions are ruled out. Definitive proof that redox reactions occur by electron transfer through extended bond systems came rather late in the development of interest in this possibility, though a great deal of persuasive evidence based on rate comparisons had been offered,^{5,25,30,31} and though claims of proof were made some time ago^{32,33} (but see ref 34). Partly because the history of this subject is somewhat cloudy, it seems desirable to outline, for at least one system, the evidence⁶ for remote attack as a path for oxidation-reduction.

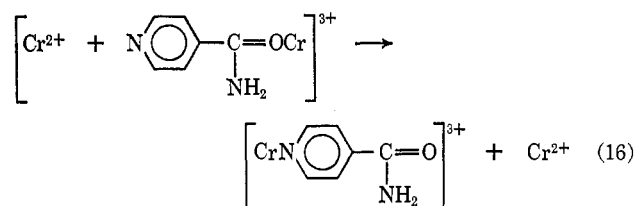
The reaction of VII with Cr^{2+} ($k_0 = 4.0 \times 10^{-3} M^{-1} \text{sec}^{-1}$ at 25°) yields $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ as the only Cr(III) product. That of VIII with Cr^{2+} is much more rapid



($k_0 = 17.4 M^{-1} \text{sec}^{-1}$ at 25°) and the first Cr(III) product observed is IX. The fact that Cr(III) in the product is found attached to the remote end of the isonicotinamide ligand, taken alone, does not prove that Cr^{2+} attacks this position. We must rule out the possibility that a different species is initially formed, and that it rearranges spontaneously or under the influence of Cr^{2+} to the product observed. The combination $[\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{free ligand}]$ is excluded as an intermediate stage, because it, in fact, represents the final stable state for the Cr(III) products. The possibility of primary attack at the pyridine nitrogen followed by rearrangement is rendered unlikely by comparing rates and products with those observed for the pyridine complex (no ligand transfer occurs for the latter), but, in any event, is dealt with by the observations which will now be described. Although IX is formed first in the reaction of Cr^{2+} with VIII, when the former reactant is in excess, X appears among the products, and to an in-



creasing extent as (H^+) is lowered. The spontaneous transformation of IX to X is slow, much slower than the irreversible loss of ligand by aquation. The detailed study of the product mixture shows Cr^{2+} to be an efficient catalyst for the change of IX to X, and by a process which must also involve remote attack (eq 16).



Whenever the characterization of an intermediate Cr(III) product is used to diagnose mechanism, rearrangement of the intermediate under the influence of Cr^{2+} must be taken into account. Clearly, in the present system, rearrangement of IX to X does occur, but by the secondary process (16). The species IX is the primary product; hence, VIII is reduced by Cr^{2+} by remote attack.

There is no evidence on hand for electron transfer through extended saturated bond systems. This does not mean that such a process is impossible, but rather that some alternative process, such as outer-sphere reduction, competes favorably against remote attack through saturated bond systems.

It may next be asked whether a conjugated bond system which provides a suitable "remote" polar group ensures facile electron transfer by remote attack. Such a question is especially significant when approximately equivalent sites lie at remote and adjacent positions.

The reductions, with $\text{Cr}^{2+}(\text{aq})$, of complexes XI⁶ and XII^{5,35} are of interest here. Not only are the rates and

(29) H. Taube, "Mechanism of Inorganic Reactions," *Advances in Chemistry Series*, No. 14, American Chemical Society, Washington, D. C., 1965, p 107.

(30) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

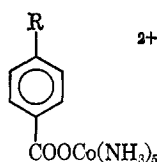
(31) See Table I, footnote d.

(32) R. T. M. Fraser, D. K. Sebera, and H. Taube, *J. Am. Chem. Soc.*, **81**, 2906 (1959).

(33) R. T. M. Fraser and H. Taube, *ibid.*, **81**, 5000 (1959); **83**, 2242 (1961).

(34) J. K. Hurst and H. Taube, *ibid.*, **90**, 1178 (1968).

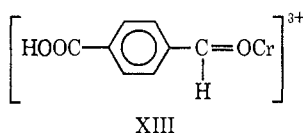
(35) A. Zanella, work in progress.



XI, R = COOH; $k = 0.20$
 XII, R = CHO; $k = 54 + 3.8 \times 10^2(H^+)$

rate laws different, but the chemistry is different as well. Ligand transfer is virtually complete for reduction of the terephthalato complex XI, but with the aldehyde derivative XII the parent ligand is found free in solution.

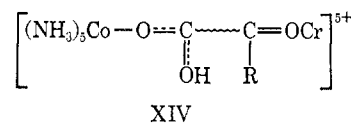
The kinetic results indicate that something unusual is happening with XII, but not with XI. The release of the aldehyde ligand from XII is thought to result from aqation of the primary product, XIII. Hydrolysis of a species such as XIII would be expected to proceed by carbon-oxygen, rather than by chromium-oxygen, bond breaking and should be rapid, as are substitution reactions by water at $>C=OH^+$ centers,³⁶ which are structurally analogous to $>C=OCr^{3+}$. Indeed, rapid-flow studies of the reduction of XII detect³⁵ a labile intermediate which may reasonably be taken as a chromium(III) aldehyde product, XIII.



It appears then that there is little, if any, remote attack in reduction of the terephthalato complex XI, but when an aldehyde group is substituted for COOH, remote attack is much more facile than adjacent attack (which may be presumed to proceed at a specific rate of about $0.2 M^{-1} sec^{-1}$, the approximate value for many substituted benzoato complexes). The aldehyde group may have a slight advantage over the carboxy in the stability of the precursor complex, but this almost certainly cannot be the main cause of the rate differences, and in any case the difference in the form of the rate laws cannot be explained in terms of the concentration of the precursor complexes. Once again, it is suggested that the difference in rate by the k_0 path can be ascribed to the difference in the energy of a low-lying, unoccupied orbital for the two ligands. This difference, though not documentable quantitatively, is again indicated by the greater ease of reducibility of a formyl group compared to a carboxyl group.

A reaction path featuring a first-order hydrogen ion (k_h) term has been observed also with fumarate³¹ and muconate^{37,38} as ligands, and it has been reported also³¹ for oxalate and maleate,³⁹ though subsequent work^{9,38,40} has shown that the k_h term is not important for the latter two.

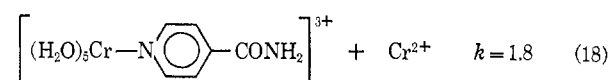
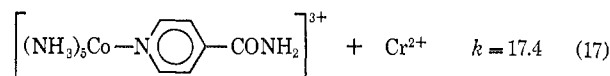
The participation of H^+ in the electron-transfer reaction by the k_h path is in accord with reaction *via* remote attack. It can be supposed that the additional proton lies on the Co(III)-bound carboxyl group as in structure XIV. In this position, the proton in the activated



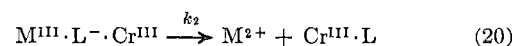
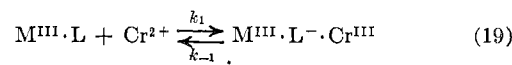
complex conceivably improves conjugation between the lead-in oxygen and the extended conjugated bond system. This explanation of the role of H^+ , though plausible, is not unique. Attachment of a proton may also lower the energy of the unoccupied orbital which is presumably involved in the electron-transfer process. We cannot say which effect is the more important, and there may well be others.

Electron Transfer to Ligand as Rate Determining.

The reactions of Cr^{2+} with $(NH_3)_5CoF^{2+}$ ⁴¹ and $(NH_3)_5CoOH^{2+}$ ⁷ are several million times as rapid as with the corresponding $(H_2O)_5Cr^{3+}$ systems.^{15,42} The electron-transfer processes are thought to be similar for both pairs of oxidants; the incoming electron is absorbed into an antibonding d orbital having σ symmetry, and inner-sphere mechanisms operate in all four cases. Almost certainly the Co(III) complexes are reduced more rapidly because the thermodynamic driving force is much greater. Kinetic analysis of the reaction of Cr^{2+} with the pyridine derivative VII has yielded⁸ specific rates for the processes 17 and 18. Moreover, for the reduc-



tion of XV, $k_0/2$ (note the two equivalent sites for attack) is observed to be $7 M^{-1} sec^{-1}$.⁴³ *The small rate differences among complexes of reducible ligands thus contrast markedly with differences in rates with simple bridging ligands*, and this suggests that with reducible ligands electron transfer from Cr^{2+} to the ligand is rate determining, or nearly so, for the reduction of the oxidizing metal ions. A stepwise mechanism of this sort is given by eq 19 and 20. Here, k_0 is given by the func-



tion $k_1 k_2 / (k_{-1} + k_2)$. When k_{-1} is similar in size to k_2 or smaller (that is, if the radical-ion intermediate usually decays to products rather than returning to reactants),

(36) M. L. Ahrens and H. Strehlow, *Discussions Faraday Soc.*, **39**, 112 (1965).

(37) F. Nordmeyer and D. K. Sebera, unpublished observations.

(38) See Table I, footnote e.

(39) R. T. M. Fraser, *J. Am. Chem. Soc.*, **85**, 1747 (1963).

(40) M. V. Olson, Y. Yamamoto, and H. Taube, to be published.

(41) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

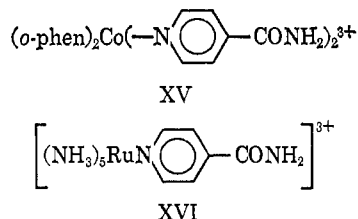
(42) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(43) F. Maspero and J. Taube, unpublished observations.

k_0 will be $\sim k_1$. In the absence of special effects (see below) the coefficient k_1 is not expected to be sensitive to the nature of the associated metal ion.

Effect of Electronic Structure of the Metal Ion on Rates of Electron Transfer. The path described above for reducible ligands is, in effect, a chemical mechanism for electron transfer; the ligand is converted to a radical ion which then usually decays by reducing the oxidizing metal ion. This type of mechanism is not proven by the observations cited, but it is strongly suggested by them, and, moreover, it is consistent with the chemistry of isonicotinic acid derivatives. Radical ions have been shown⁴⁴ to be remarkably stable for them, and the radical-ion state may well be within reach of a reducing agent as strong Cr^{2+} ($E^\circ_{\text{Cr}^{3+}, \text{Cr}^{2+}} = -0.45 \text{ V}$). Recall that with F^- as a bridging ligand, a chemical mechanism for the redox process is ruled out energetically; here the electron transfers by penetrating, rather than by surmounting, the energy barrier. Further evidence shows that the pattern established for the isonicotinamide complexes of Co(III) and Cr(III) does not, with out modification, extend to all metal complexes of this ligand.

Although the driving force for the reaction of Cr^{2+} with XVI is little different from that of the corre-



sponding aminocobalt(III) complex, the Ru(III) complex is reduced 30,000 times as rapidly as the Co(III) derivative.⁴⁵ In both cases, reduction proceeds *via* remote attack, with the Cr(III) remaining bound to the amide group in the primary product. The sizable enhancement in the case of Ru(III) is thought to reflect the character of its acceptor orbitals. The ions Co(III) and Cr(III) have the electronic structures $t_{2g}^6e_g^0$ and $t_{2g}^3e_g^0$, so that in each case the electron added when the metal ion is reduced enters an e_g antibonding orbital. This orbital has σ symmetry with respect to the metal-ligand bond, and therefore does not overlap effectively with the π orbitals of the ligand. Ru(III) has the electronic structure t_{2g}^5 , and the incoming electron now enters an orbital which overlaps effectively with the π ligand orbitals.

The apparent stepwise nature of the electron-transfer act for the Co(III) and Cr(III) complexes suggests that since the final acceptor orbital is too distant for direct overlap with the donor orbital, the electron first enters a low-lying π orbital of the ligand. Before it can pass to the metal acceptor center, a distortion in the coordination sphere of the metal must occur to lower the energy

of the σ acceptor orbital (which is antibonding) and to provide some overlap with the half-occupied π orbital of the ligand radical ion. When Ru(III) is the acceptor, the molecular orbital which the electron will finally occupy includes the ligand, though because of the energy difference of the t_{2g} metal orbital and the ligand orbital of matching symmetry, the probability of finding the electron on the ligand is low. To the extent that it is correct to say that the electron in the final state is largely centered on the metal ion, we may say that electron transfer takes place by a tunneling process, and that matching symmetry of the t_{2g} and ligand orbital reduces the barrier to electron transfer. We are tracing here as a function of location on Ru(III) *vs.* ligand the energy of the electron in the orbital which it will finally occupy ($\phi_{\text{Ru}} + \phi_{\text{L}}$) rather than in the antibonding orbital complementary to it ($\phi_{\text{Ru}} - \phi_{\text{L}}$) which will be largely ligand centered. It is suggested, but not proved, that the electron moves directly to the final acceptor orbital rather than first entering the ligand-centered, antibonding orbital.

Apart from the provisional nature of the arguments above, the observations on Co(III) and Ru(III) do suggest the orbital symmetry is an extremely important factor in determining the rate of reaction. Additional comparisons support this view. For Cr^{2+} reductions in the $(\text{NH}_3)_5\text{Co}^{\text{III}}$ series, the hydroxo complex reacts 4,000,000 times as rapidly as the acetato, but for such reductions in the $(\text{NH}_3)_5\text{Ru}^{\text{III}}$ series, the rate ratio is only 140. The relative improvement^{24b} in bridging efficiency of acetate for Ru(III) may well reflect the matching of the symmetry of the acceptor orbital of Ru(III) with the π orbital of the carboxylate group. A comparison can also be offered involving reducing agents: Cr^{2+} (σ -electron donor) and V^{2+} (π -electron donor). Despite the fact that V^{2+} is the weaker reducing agent by $\sim 0.15 \text{ V}$, it reacts with CrOOCCH_3^{2+} at least 10^3 more rapidly⁴² than does Cr^{2+} . Here again it seems likely that we are looking at effects due to differences in orbital symmetry.

General Discussion

The distinction in mechanism of electron transfer through conjugated bond systems in the preceding section can be summarized in the following way: when Co(III) is the acceptor and the bridging ligand is reducible, electron transfer takes place to the ligand, and a particular distortion about the metal is necessary for the electron to be accepted by and trapped in the σ antibonding orbital on the acceptor metal ion. With Ru(III) , transfer takes place directly to the acceptor orbital and is facilitated by the favorable overlap between the final acceptor orbital and the π orbital of the ligand.

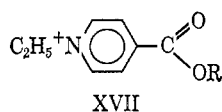
Electron transfer by tunneling, as suggested for Ru(III) , is, in principle, possible also for Co(III) , but empty ligand orbitals of symmetry needed to mix with the acceptor σ orbitals of Co(III) lie extremely high in energy, and the chemical mechanism by "electron hopping" is more facile.

(44) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963).

(45) R. G. Gaunder and H. Taube, to be published.

When the ligand is not so easily reduced, the hopping mechanism is excluded, as is the case for the fluoride bridge, and probably also for acetate and benzoate.

Considering the acetate case in detail, the over-all specific rate for the electron-transfer reaction k_0 must be equal to or less than the product $k_t K_p K_r$, where k_t refers to decay of the radical-ion intermediate state to product, K_p is the equilibrium constant for the formation of the precursor complex, and K_r is the equilibrium constant for the conversion of this complex to the state $\text{Co}^{\text{III}}\text{OOC-CH}_2\text{-}\dot{\text{C}}\text{r}^{\text{III}}$. If we set k_t at the maximum value of 10^{13} sec^{-1} and estimate K_p as $1/55$ (this is equivalent to no discrimination between water or carboxylate at the sixth coordination position on Cr^{2+}), K_r is calculated as $>10^{-12}$. The limit on K_r requires E° for the couple $\text{CH}_3\text{COOH} + e^- \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}^-$ to be less negative than -1.2 V , and this seems entirely unreasonable in view of the difficulty of reducing acetic acid.⁴⁶ If k_t is less than 10^{13} sec^{-1} , reduction to the radical ion must be even more facile. Because of the weak discrimination shown by Cr^{2+} between oxygen ligands, the estimate of K_p is probably not off by more than a factor of 10. Using a proton as in the couple shown above instead of the metal ions on acetate, if anything, favors reduction of acetate. This analysis, although approximate, would appear to rule out a chemical mechanism when acetate is the bridge; a mechanism similar to that for the fluoride bridge is more likely. In view of the known⁴⁴ ready reducibility of XVII a chemical mech-



anism when a pyridine derivative is the bridging group remains quite reasonable.

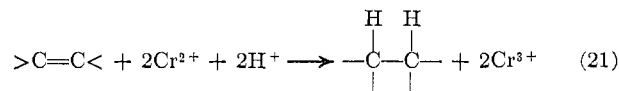
Ligand reducibility should be considered also in connection with effects arising from a conjugated system in a pendant position. In the Cr^{2+} reduction of $\text{Co}(\text{NH}_3)_5$ complexes of various fumarate derivatives, only small changes of k_0 result when the unbound carboxyl group is converted to an ester or an amide,^{31,34} whereas the k_h terms are sensitive to such changes. This suggests that the k_0 paths reflect reduction by adjacent attack. If so, a modest pendant group effect operates for fumarate derivatives ($k_0 = 1.4$ compared to 0.35 for $\text{CH}_3\text{-CO}_2^-$) even in the nonchelate case. When maleate is the ligand, the k_0 path contributes the only important term, and it now has a value of 200.^{38,40} With acid phthalate, with much the same geometry as maleate, k_0 is again quite small,³¹ 0.08. These effects are in line with ligand reducibility, and it is unlikely, therefore, that the mechanism for the maleate is by tunneling involving the high-energy unoccupied orbital of the ligand.

Though the qualitative relation between the reducibility of a ligand and its capacity to mediate in electron transfer to $\text{Co}(\text{III})$ is consistent with the radical-ion

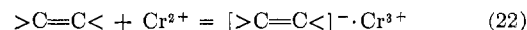
mechanism, note that it is also consistent with a resonance-transfer mechanism and therefore does not constitute added proof of the radical-ion mechanism. With the proper distortion about $\text{Co}(\text{III})$ and $\text{Cr}(\text{II})$, there can be some overlap between ion-centered orbitals and an unoccupied π orbital of the ligand, and electron transfer could then take place directly from $\text{Cr}(\text{II})$ to $\text{Cr}(\text{III})$. This mechanism seems improbable because it requires coincidence of independent events, each of low probability. It cannot be eliminated, however, by *a priori* reasoning, and we favor the stepwise process on experimental grounds, *i.e.*, the observed variation of rates as the acceptor center is changed. Proof of this mechanism is by no means absolute, and effort needs to be devoted to detecting radical-ion states for the bridging group by physical or chemical means.

The preceding discussion suggests that patterns are beginning to appear in the relation between the electronic structure of reactants and rates of electron transfer. Further experimental results along the lines described should sharpen the patterns, but extensions into new areas are also required. An obvious such extension is to combine a complex featuring a t_{2g} acceptor center with a t_{2g} electron donor as reagent. A problem here is that outer-sphere electron transfer may be very facile and may compete with the bridge mechanism, particularly in systems chosen to illuminate such possibilities as electron transfer across saturated sequences or hydrogen bonds. To inhibit outer-sphere electron transfer, effective "blocking groups" must be introduced. This may be possible by substituting bulky alkyl groups for hydrogen on coordinated ammonia, but the systems will have to be chosen with care for, at least in some cases, sterically demanding substituents have been found to accelerate outer-sphere reduction.⁴⁷ Another way to examine relations between reactivity and orbital symmetry is to investigate nonoctahedral complexes. Pentacoordinate (trigonal bipyramidal) complexes should be particularly interesting, but much ingenuity will be required to devise systems which will furnish decisive tests of mechanism.

It has already been emphasized that qualitative comparisons between ligand reducibility and rate of electron transfer do not allow a clear-cut choice between two suggested mechanisms. A quantitative relation may prove more useful, and for this reason, among others, there is a need for a precise measure of reducibility. The relationship between the rate of the reduction (eq 21), which,



up to now, has been used as a measure of reducibility, and the energy change for the process (eq 22), though



possibly helpful in qualitative comparisons, is by no means exact. Reversible one-electron redox potentials

(46) L. Meites, "Polarographic Technique," Interscience Publishers, New York, N. Y., 1967.

(47) Y. Wang and E. S. Gould, unpublished experiments. See also E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).

for the ligands would undoubtedly be more pertinent than are the rates of reactions such as (21) but may be impossible to determine in reducible proton-labile solvents. Closest to the mark might be a method of measuring the energy of transferring an electron abruptly from some common source to the ligand carrier orbital of the proper symmetry. There is some hope that for a series of ligands, such as nitrogen heterocyclics, the energy of the band maximum for the electron-transfer transition⁴⁸ in the complexes with $(\text{NH}_3)_5\text{Ru}^{2+}$ will serve. The transition in question undoubtedly involves transferring an electron from the t_{2g} levels of Ru to an acceptor level on the ligand, having π symmetry matching that of the t_{2g} electrons of Ru. With judicious choice of ligand, and of substituents, series can be devised to expose the relationship between the energy of the unoccupied levels of the ligands and the rates of electron transfer.

The present Account has stressed observations, but the development of the subject nevertheless has been guided by theoretical considerations. In addition to publications, already mentioned, dealing with the

(48) P. C. Ford, DeF. P. Rudd, R. G. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

theory of electron transfer through bridging groups, the reader is referred to a paper⁴⁹ in which the Halpern and Orgel¹³ treatment is extended to include effects other than those arising from bond conjugation, a paper by Libby⁵⁰ emphasizing the relevance to the reactions of the Franck-Condon restrictions, and a more general treatment in book form⁵¹ of the entire subject of electron-transfer reactions. The book provides breadth of coverage, useful for placing the material in the present Account into the context of the subject as a whole; it is also recommended for the clear development of the basic principles and for the care with which the present limitations of quantitative approaches are stated. The quantitative treatment of the complex behavior is difficult, at best, and it has not been helped by the experimental errors which have confounded the subject in its formative stage. It is too much to hope for a complete quantitative treatment at the present time, but some advances toward a quantitative theory can perhaps be based on the experimental results now being generated.

(49) P. V. Manning, R. C. Jarnagin, and M. Silver, *J. Phys. Chem.*, **68**, 265 (1964).

(50) W. F. Libby, *J. Chem. Phys.*, **38**, 420 (1963).

(51) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," The Ronald Press, New York, N. Y., 1966.

Kinetics of Organic Reactions in Micellar Systems

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The chemical literature in the period 1900–1958 contains a scattering of reports concerning reaction kinetics in aqueous media containing ionic or nonionic surfactants.¹ However, substantial insight into this area was first achieved in 1959 by Duynstee and Grunwald in their study of the effects of cationic and anionic surfactants on the rate of alkaline fading of cationic triphenylmethane dyes.² Since that time, related studies have been appearing at an increasing rate, and interest is still growing.

Surfactants are amphipathic molecules having both pronounced hydrophobic and hydrophilic properties. Such molecules have the important property of forming over a certain small concentration range, termed the critical micelle concentration or cmc, molecular aggregates, called micelles. It is the micelles, rather than individual surfactant molecules, which are responsible for altering the rates of organic reactions in aqueous solutions of surfactants. What has generally been observed is that the proper choice of surfactant can lead

to rate increases of 5- to 1000-fold compared to the same reaction in the absence of surfactant. Typically, rate increases of 10- to 100-fold are elicited by surfactant concentrations near 0.02 *M*.

Although so far not more than 50 directly relevant publications have appeared in this field, several important generalizations and conclusions seem warranted. Furthermore, a good many avenues open for exploration are now apparent. This brief review attempts both to summarize these conclusions and to point the way to these avenues. As is customary in these pages, emphasis is placed on developments in our own laboratory, and we have deliberately avoided producing a comprehensive survey.

Motivation for adding surfactants to mixtures of chemical reactants, usually organic in nature, may be considered to derive from three sources: first, to further understanding of those factors which influence the rates and courses of organic reactions; second, and closely related to the first, to gain additional insight into the exceptional catalysis characteristic of enzymatic reactions; third, to explore the utility of micellar systems for the purpose of organic synthesis. At the moment, the last of the factors remains completely unexplored and the second largely a matter of speculation.

(1) For a summary of early work and an exhaustive compilation of studies in this field through early 1968, see: R. B. Dunlap, Ph.D. Thesis, Indiana University, 1968.

(2) E. F. J. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, **81**, 4540, 4542 (1959).